NMR SPECTROSCOPY OF SOME NITROGEN-BORON COMPOUNDS

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REVIEW OF THE LITERATURE

The nitrogen-boron grouping is isosteric and isoelectronic with a carbon-carbon grouping (1). For this reason aminoboranes have been compared with analogous ethylene compounds. It is of considerable interest as to how far such an analogy can be carried. Of particular interest is the extent of double-bond formation between nitrogen and boron and how such double-bonding affects the physical and chemical behavior of the aminoboranes. For example, if the double-bond character is sufficiently high, *cis*-*trans* isomerism of unsymmetrically substituted aminoboranes might be observed.

During the past few decades considerable work has been done on trying to estimate the extent of double-bond formation between nitrogen and boron in aminoboranes. In the next few pages the literature findings on this subject will be briefly reviewed.

Early Indications of N-B Double Bond Character

In 1948 Wiberg (2) postulated aromatic character for borazine on the basis of some physical constants. The observed N-B bond length is between that of a double bond and a single bond. The observed value of the parachor for borazine is between that calculated for a single-bonded and that for a double-bonded species. In benzene, the large discrepancy between the calculated and observed vibrational frequency of the non-planar C-H deformation mode is believed to be due to the aromatic character of benzene. Such a large discrepancy exists between the observed and the calculated vibrational frequencies of the B-H or N-H non-planar deformation mode in borazine.

Further spectroscopic investigations indicated that there is appreciable N-B double-bond character in non-cyclic nitrogen-boron compounds also. Aubrey's (3) IR studies on borazenes showed that the B-N asymmetric stretching vibration is of higher frequency than the same vibration for B-O in boric esters. Aubrey attributes this to greater pπ-pπ overlap between B-N than between B-O.

The N-H stretching frequency in borazenes indicates that there is little intermolecular hydrogen bonding. There must be appreciable double bond character between the boron and nitrogen, thus reducing the basicity of the nitrogen.

Niedenzu and Dawson (4) in 1960 proposed the existence of cis-trans isomers in unsymmetrically substituted aminoboranes. Some of their evidence for cis-trans isomerism was: (1) There are found two and only two "modifications" of the unsymmetrically substituted aminoboranes; (2) molecular weights of the "modifications" indicated identical empirical formulae; (3) rupture of the N-B bond always yielded the secondary amine that was used as the starting material; (4) equilibration between the "modifications" was very rapid, occurring at room temperature without further supply of energy. The sum of this evidence rules out inter- or intra-molecular disproportionation, but leaves hindered rotation about the N-B bond as the cause of the observed "modifications."

Magnetic Non-equivalence of Some Aminoborane Substituents

In 1961, Ryschkewitsch, Brey and Saji (5) demonstrated the existence of magnetically non-equivalent boron methyls in $CH_3(C_6H_5)N$-$B(CH_3)_2$. The NMR spectrum of this compound at room temperature shows two BCH_3 peaks, which correspond to the magnetically non-equivalent boron methyls cis and trans to the phenyl. The phenyl substituent on nitrogen is sufficiently magnetically anisotropic so as to cause the shielding of the BCH_3 cis to the phenyl to be appreciably different from the BCH_3 trans to the phenyl.

As the temperature was raised, the BCH_3 peaks broadened and finally merged at 100°. At still higher temperatures the single peak became more narrow. Such behavior of the NMR spectrum is characteristic of intramolecular rotation when the rate of rotation varies with temperature.

Dimeric forms of the aminoborane cannot explain the observed spectrum and its temperature dependence. The molecular weight indicated the monomeric form of the compound. The authors were able to make a preliminary estimate of the barrier to rotation as 15 ± 3 kcal/mole and of the lifetime in the individual molecular states as 10^{-2} sec at 100°C.

A little later the same year, Barfield, Lappert and Lee (6) reported non-equivalence of the NCH_3 peaks for $(CH_3)_2N\text{-}B(C_6H_5)Cl$. The spectrum of the compound showed two NCH_3 peaks at room temperature; the peaks merged at 118°C. The activation energy for the hindered rotation was estimated as 14 kcal/mole. Lappert (7) later demonstrated that the NCH_3 non-equivalence in this compound was due to a shift difference by running the compound at 40 and 60 Mc. The peak separation at 40 Mc was two-thirds of that found at 60 Mc.

Further Aminoboranes with Magnetically Non-equivalent Substituents

In the subsequent years, non-equivalence of either the N or the B substituents has been observed in a number of aminoboranes. For example, Lappert (7) obtained for the non-equivalent NCH_3 peaks of $(CH_3)_2N\text{-}B(C_6H_5)Br$ a coalescence temperature of 118°C and an activation energy of 21.0 ± .7 kcal/mole. The activation energy of the chloro analogue had been found to be 14.0 ± .8 kcal/mole (6,7). The higher barrier to rotation in the bromo case is attributed to the lessened ability of the bromine to π-bond with the boron.

When the most efficient π-donor halogen, fluorine, is substituted on the boron, no NCH_3 doublet was observed even at -50°C. The size of the halogen could also affect the ease of rotation about the N-B bond.

Lappert also observed NCH_3 non-equivalence in $(CH_3)_2N\text{-}B(C_6H_5)CH_3$. This observation has subsequently been confirmed by Totani (8) and Becher (9). The coalescence temperature for this compound was found to be 99.5°C. Lappert also found non-equivalence of NCH_3 for $(CH_3)_2N\text{-}B(C_6H_5)OCH_3$. For this compound the merging temperature was +37° and the barrier to rotation 16 kcal/mole. The high activation energy of this compound as compared to the chloro analogue is surprising, since oxygen is considered to be a better electron pair donor than chlorine. Possibly steric effects of the substituent may be important.

Lappert also found non-equivalence of the NCH_3 protons for $CH_3(C_2H_5)N\text{-}B(C_6H_5)Cl$ and $CH_3(iso\text{-}C_3H_7)N\text{-}B(C_6H_5)Cl$. The activation energy for the former was estimated as 11.5 or as 12.3 kcal/mole, depending on what method of calculation was used. The isomer ratio for $CH_3(C_2H_5)N\text{-}B(C_6H_5)Cl$ was 1:1, while that for $CH_3(iso\text{-}C_3H_7)N\text{-}B(C_6H_5)Cl$ was 3:4.

Lappert could not detect a second NCH_3 peak even at -50°C for $[(CH_3)_2N]_2BC_6H_5$ or for $CH_3(C_6H_5)N\text{-}B(C_6H_5)Cl$. The same broad NCH_3 signal at room temperature was observed for the latter compound as had been found by Brey _et al_. (10).

Brey, Fuller, Ryschkewitsch, and Marshall (10) had refined their earlier estimate of the barrier to rotation in $CH_3(C_6H_5)N-B(CH_3)_2$ and obtained 10.8 + .7 kcal/mole as the new value. The frequency factor for the rotation was estimated to be 2.9×10^8 sec^{-1}. The authors point out that these values of the activation energy and frequency factor are very close to those found by Rogers and Woodbrey (11) for N,N-dimethylacetamide.

Brey et al. have been able to observe cis-trans isomerism in $CH_3(C_6H_5)N-B(C_6H_5)CH_3$. Both the NCH_3 and the BCH_3 peaks are non-equivalent below room temperature. The isomer in larger abundance has the methyl resonances to higher field. Models indicate that in the trans isomer the methyls would be more shielded, therefore the trans isomer must be in greater abundance. The authors observe that the trans isomer in dimethylstilbene has been found to be the energetically favored isomer (12,13).

The natural log of the peak area ratio of the two isomers in $CH_3(C_6H_5)N-B(C_6H_5)CH_3$ has been plotted versus the inverse of the absolute temperature. The plot gave a slope at room temperature which corresponds to an enthalpy difference of 1.7 ± .5 kcal/mole between the two isomers.

For this compound the NCH_3 peaks merge at +75° with a τ value of 6.90, while the individual NCH_3 peaks of the two isomers have τ values of 6.80 and 6.90 at -25°C. Thus the merged NCH_3 peak at +75°C does not have the concentration-weighted average shift of the isomers. The unexpected behavior of the NCH_3 resonances is attributed to a changed chemical shift in one or both of the isomers with changing temperature. Such a change "is reasonable if the weakening of the pi N-B bond leads to a change in the hybridization of the nitrogen atom, with possible loss of planarity of the bonds surrounding the nitrogen." The merged BCH_3 peak has the concentration-weighted average of the separate isomers.

Brey *et al.* observed non-equivalent NCH_3 and NCH_2 peaks in $CH_3(C_6H_5CH_2)N\text{-}B(C_6H_5CH_2)C_6H_5$. The relative intensity ratio was 1.54 for the NCH_2 peaks and 1.23 for the NCH_3 peaks. The BCH_2 showed a single peak. There was no change in the spectrum from -25° to +75°.

Totani, Watanabe and Kubo (8) observed non-equivalence of the BCH_3 peaks in the series of compounds $R(C_6H_5)N\text{-}B(CH_3)_2$, where R was methyl, ethyl, isopropyl and tertiary-butyl. The chemical shifts of the low-field BCH_3 peaks remained almost unaffected by the nature of the alkyl, while the shifts of the up-field BCH_3 peaks increased with increasing size of the alkyl group. Earlier work of Becher and Frick (14) has shown that the phenyl group must be increasingly skewed out of the molecular plane with increasing size of the alkyl group. The more nearly the plane of the phenyl ring is at a right angle to the plane of the molecule, the more the phenyl ring-current will shield the methyl group cis to the phenyl, while the methyl group trans to the phenyl will remain essentially unaffected. Totani et al. therefore conclude, that for their series of compounds the up-field BCH_3 signals must be due to the BCH_3 cis to the phenyl, while the low-field signals must be attributed to the BCH_3 trans to the phenyl.

Non-equivalence of the NCH_3 signals for the series of compounds $(CH_3)_2N-B(C_6H_5)R$, where R was methyl, ethyl, isopropyl, isobutyl and tertiary butyl, has also been observed by Totani et al. The same effect of the size of the alkyl group on the shielding on the methyl groups was found as for the BCH_3 series. By the same reasoning the authors attribute the up-field methyl peak to the methyl cis to the phenyl.

Totani et al. further observed non-equivalence of the NCH_3 for $(CH_3)_2N-B(C_6H_5)Cl$. While Brey (10) and Lappert (7) saw only one NCH_3 peak for $CH_3(C_6H_5)N-B(C_6H_5Cl$, Totani et al. report seeing two NCH_3 peaks of area ratio 31:9. Totani et al. obtained IR spectra of this compound. The spectrum obtained of a sample rapidly cooled after heating to 250°C differs somewhat from the spectrum obtained of an unheated sample. On leaving the heat-treated sample at room temperature for about a week, an identical spectrum was obtained as of an unheated sample. The authors attribute the hysteresis of the IR spectra to slow inter-conversion of cis-trans isomers of the sample.

Totani, Tori and Watanabe (15) observed non-equivalence of NCH_3 peaks for $(CH_3)_2N\text{-}B(C_6H_5)C{\equiv}CCH_3$ and $(CH_3)_2N\text{-}B(C_6H_5)C{\equiv}CC_6H_5$. The barrier to rotation obtained for these compounds was 21 kcal/mole and 19 kcal/mole, respectively. For $(CH_3)_2N\text{-}B(C_6H_5)C_2H_5$ the activation energy of the hindered rotation was found to be 19.7 kcal/mole. Cis-trans isomerism was observed in $CH_3(C_6H_5)N\text{-}B(CH_3)Cl$ and in $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH_3$. Totani, Tori, and Watanabe estimated the barrier to rotation to be 13 kcal/mole and 15 kcal/mole, respectively. Non-equivalence of $CH_3(C_6H_5)N\text{-}B(CH_3)Cl$ had previously also been observed by Totani et al. (8,16).

Baechle and Becher (17) observed cis-trans isomerism in $CH_3(C_6H_5)N\text{-}B(CH_3)OC_2H_5$. The NMR spectrum of this compound showed two NCH_3 and two BCH_3 peaks. The intensity ratio was estimated to be between 1:10 and 1:20. Of the $BOCH_2CH_3$ group, only the CH_3 appeared to be non-equivalent, but not the CH_2. Baechle and Becher attribute this to the fact that the preferred orientation of the OCH_2 is along the N-B axis, and thus the CH_2 is not shielded differently by the phenyl ring current in the cis and trans forms.

Above 120°C the peaks for the non-equivalent groups broadened, but did not merge yet. Hysteresis of the NMR spectrum was observed. The spectrum of a sample which had been rapidly cooled from 120° to 20°C showed increased peak size for the less abundant isomer. Re-equilibration at room temperature took several hours.

No indication of cis-trans isomers could be observed in either the IR or the Raman spectra.

For phenyl substituted aminoboranes, Becher and Baechle (18) have been able to correlate the observed CH_3 chemical shifts with those obtained from calculations, assuming a skew angle for the phenyl group.

The effect of a phenyl ring on the chemical shift of neighboring protons has been calculated by Becher and Baechle following the method of Waugh and Fessenden (19), and Johnson and Bovey (20). Bond angles of 120° for both N and B, also coplanarity of all N and B bonds, were assumed. Known bond lengths of N-B compounds were used. The authors varied the skew-angle between the phenyl ring and the N-B bond plane, and for each value of the angle calculated the change in shielding for the methyl protons.

By comparing the observed change in shift on phenyl substitution with a plot of the calculated change in shielding versus the skew angle, it should be possible to obtain a skew angle for the given compound. The difficulty with this approach might be that phenyl substitution could affect the bonding character of the N-B bond and thus influence the methyl shift. But by using the shift difference between the two BCH_3's in $CH_3(C_6H_5)N\text{-}B(CH_3)_2$, the effect of phenyl substitution on the bonding is automatically eliminated. Using the experimental chemical shift difference between _cis_ and _trans_ BCH_3 of the above compound, the authors' plot yielded a phenyl skew angle of 60 ± 2° for phenyl on nitrogen. By using the value thus obtained for the skew angle, Becher and Baechle were able to predict the shifts of the BCH_3's in $(C_6H_5)_2N\text{-}B(CH_3)_2$ and the shift of the NCH_3 in $CH_3(C_6H_5)N\text{-}B(CH_3)_2$. The predicted values agree to 0.1 ppm or better with the observed values.

Using the same procedure, Becher and Baechle obtained a skew angle of 48° for $(CH_3)_2N\text{-}B(C_6H_5)CH_3$ and were able to predict the NCH_3 shift of $(CH_3)_2N\text{-}B(C_6H_5)_2$ to 0.05 ppm. Similarly the NCH_3 and BCH_3 shifts for $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH_3$ are predicted to 0.1 ppm.

However, no _cis_-_trans_ isomers could be observed in the infra-red spectrum of this compound (21). Also, the NCH_3 peaks in the NMR spectrum merge at 75°C, which is considerably lower than the 120°C temperature observed by Baechle and Becher (17) for the peak broadening of $CH_3(C_6H_5)N\text{-}B(OCH_2CH_3)CH_3$.

For these reasons Becher and Baechle proposed that the two magnetically non-equivalent forms of $CH_3(C_6H_5)N\text{-}B(CH_3)C_6H_5$ are not due to cis-trans isomerism, but rather to forms of the trans isomer which have the phenyl groups skewed out of the plane and which also have tilting about the N-B bond.

Becher and Baechle assume restricted rotation about the N-B bond and also about the $N\text{-}C_{aryl}$ and $B\text{-}C_{aryl}$ bonds. With these assumptions one obtains four different molecular forms, but only two different magnetic environments for the NCH_3 and the BCH_3. Thus one still expects to see only two NCH_3 peaks and two BCH_3 peaks.

Becher and Baechle make no mention of the cis form, but since only two resonances are observed for each of the methyls, the cis form must either be energetically highly unfavored or the shifts in the cis form must exactly coincide with those of the trans forms. It appears to the writer that the latter condition would be quite improbable. Neither seems the complete freezing out of the cis form, even at +125°C, more reasonable than the observed rather low merging temperature of 75°C. Lappert (7) has observed a merging temperature of 99.5°C for $(CH_3)_2N\text{-}B(C_6H_5)CH_3$ and 37°C for $(CH_3)_2N\text{-}B(C_6H_5)OCH_3$.

It appears to the writer that lack of cis-trans isomers in the IR spectrum, while noteworthy, does not seem proof enough that such isomers could not be observed in the NMR spectrum of $CH_3(C_6H_5)N-B(C_6H_5)CH_3$. As Baechle and Becher (17) say for $CH_3(C_6H_5)N-B(CH_3)OCH_2CH_3$: "Since the vibration frequencies of the two forms will be largely the same or at least very close together, it is understandable that with such different population ratios no indication for the existence of two isomers can be found in the Raman or IR spectra of the compound."

However, in their later article Becher and Baechle (18) go on to calculate for $CH_3(C_6H_5)N-B(C_6H_5)CH_3$ the expected change in shielding for various values of the skew angle about the N-B bond and about the $B-C_{aryl}$ and $N-C_{aryl}$ bonds. If the authors assume that the N-B skew angle is no greater than 45°, they obtain a value of 55° for the phenyl skew angles and 40° for the N-B skew angle to give the observed shielding of the BCH_3. To account for the observed NCH_3 shifts, the authors obtain 10° for the N-B skew angle. Thus the agreement between the two methods is rather poor.

For $CH_3(C_6H_5)N-B(C_6H_5)_2$, the value predicted for the shift change agrees to better than 0.1 ppm with the observed value. Due to technical difficulties, Becher and Baechle were unable to cool the sample below 20°C. Thus they could not observe the two NCH_3 resonances which may result at low temperatures, if, again, restricted rotation about the same three bonds is proposed.

Becher and Baechle were able to prepare a mixture containing mostly $(C_6H_5)_2N\text{-}B(C_6H_5)_2$, about 10 per cent $(C_6H_5)_2N\text{-}B(C_6H_5)CH_3$ and even less $(C_6H_5)_2N\text{-}B(CH_3)_2$. The NMR spectrum of a CCl_4 solution of the mixture gave, besides the strong phenyl absorption and an absorption at 9.61 τ, attributed to the BCH_3's in $(C_6H_5)_2N\text{-}B(CH_3)_2$, two further small peaks at 9.37 and 9.18 τ. These have been assigned to the BCH_3 in $(C_6H_5)_2N\text{-}B(C_6H_5)CH_3$.

Substituent Effects and the Barrier to Rotation

The IR studies of Becher (9) and of Baechle (17) indicate that replacing an alkyl group on boron by a chlorine increases the N-B double bond character. These authors attribute the higher frequency of the N-B vibration in the chloro-substituted aminoborane to increased N-B bond order. Becher's and Baechle's IR studies further show that replacement of an alkyl by an aryl group on either the nitrogen or the boron decreases the N-B bond order, as indicated by lower frequency vibrations. Replacement of hydrogen on nitrogen by either deuterium or an alkyl group increases the N-B double bond character.

The activation energies obtained from the NMR studies show some correlation to the substituent. By comparing the activation energies of 10.8 ± .7 kcal/mole for $CH_3(C_6H_5)N\text{-}B(CH_3)_2$ (10) with the activation energy of 13 kcal/mole for $CH_3(C_6H_5)N-B(CH_3)Cl$ (15) we see that replacement of a methyl on boron by chlorine increases the activation energy. Such increase in the barrier to rotation may be due to resonance stabilization, to the inductive effect or to the steric effect of the substituent.

For compounds of the type $(CH_3)_2N-B(C_6H_5)X$, the effect of X has already been mentioned (7). Thus Lappert (7) has obtained for various X the following activation energies: Cl, 14.0 ± .8 kcal/mole; Br, 21.0 ± .7 kcal/mole; OCH_3, 16 kcal/mole; while Totani, Tori, and Watanabe (15) obtained: C_2H_5, 19.7 kcal/mole; $C{\equiv}CC_6H_5$, 19 kcal/mole; $C{\equiv}CCH_3$, 21 kcal/mole. Thus if a phenyl group and an ethyl group are attached to the boron, replacement of the C_2H_5 by Cl or OCH_3 reduces the activation energy. Replacement of the C_2H_5 on the boron by Br, $C{\equiv}CC_6H_5$ or $C{\equiv}CCH_3$ has little effect on the activation energy. Apparently when a phenyl is attached to the boron, the mesomeric effect of the other substituent is more important than its size or electronegativity.

If we compare the activation energies of 14.0 ± 0.8 kcal/mole for $(CH_3)_2N-B(C_6H_5)Cl$ (7) and 11.9 ± 0.4 kcal/mole for $CH_3(C_2H_5)N-B(C_6H_5)Cl$ (7), we see that replacement of a CH_3 on N by a C_2H_5 reduces the activation energy somewhat. This probably is due to the size of the ethyl group.

The Barrier to Rotation and the NCH_3 Chemical Shifts

The chemical shifts of the NCH_3 for compounds of the type $R(CH_3)N$-$B(C_6H_5)X$ have been plotted versus the activation energy in Figure 1. For the compounds in Figure 1, R was CH_3 or C_2H_5, while X was Cl, Br, OCH_3, $C{\equiv}CCH_3$ or $C{\equiv}CC_6H_5$. The chemical shift values and activation energy values used in Figure 1 were obtained from references 7, 8, 10, and 15.

We expect a high activation energy of the barrier to rotation to indicate efficient pπ-pπ donation from N to B. This should result in decreased electron density on the nitrogen and hence decreased shielding of the NCH_3. Figure 1 shows such a general trend of decreased NCH_3 chemical shift for large activation energy, with the exception for $X = OCH_3$ and activation energy 16 kcal/mole. Lappert (7) attributed the high activation energy in this compound to steric problems.

Insufficient data are available in the literature to make a similar plot for compounds of the type $CH_3(C_6H_5)NBXX'$ or $YY'NBXCH_3$.

Also, no data are available in the literature on B^{11} or N^{14} chemical shifts of these compounds. The boron and nitrogen shifts are expected to be much more sensitive indicators of the N-B bond order than the alkyl substituents are.

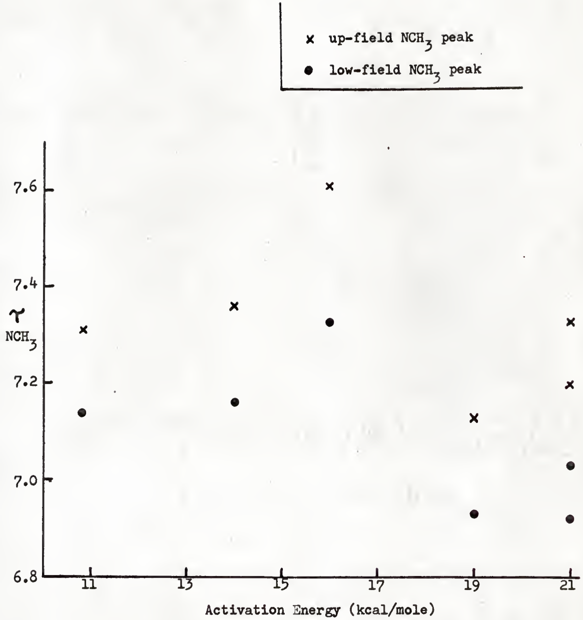


Figure 1. The NCH_3 chemical shifts and the barrier to rotation.

The NMR studies of Hawthorne (22) have shown that monomeric aminoboranes have B^{11} shifts down-field from $B(OCH_3)_3$, while dimeric aminoboranes have B^{11} shifts up-field from $B(OCH_3)_3$. Thus the boron shift should be a good indicator as to the polymeric state of the given aminoborane.

Summary of the Literature Findings

To sum up the literature findings, we note that magnetic non-equivalence of the BCH_3 and NCH_3 groups, due to restricted rotation about the N-B bond, has been observed for a number of aminoboranes. For each case of BCH_3 non-equivalence a phenyl group was attached to the nitrogen. Non-equivalence of NCH_3 was caused by either a phenyl or a chlorine on the boron.

For a number of the aminoboranes the barrier to rotation about the N-B bond has been estimated. These estimates ranged from 10.8 to 21 kcal/mole. For those aminoboranes where unequal population of isomers was observed the trans isomer appeared to be always the favored one.

The methyl chemical shifts in the aminoboranes have been correlated with the size of the other alkyl substituents and also with the phenyl skew angle. Some correlation between the substituent effects and the activation energy has been observed. The NCH_3 chemical shifts and the observed activation energy of a given compound also seem to be related.

There is some indication from IR studies that for $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH_3$ the observed magnetic non-equivalence is due to restricted rotation about the N-B, the N-C_{aryl} and the B-C_{aryl} bonds, rather than to cis-trans isomerism.

AIM OF THE INVESTIGATION

The present NMR investigation was undertaken to obtain more information about the N-B linkage in aminoboranes. It was hoped that restricted rotation about the N-B bond could be observed in some of the aminoboranes which had previously not been investigated and that the barrier to rotation for such cases could be estimated. Aminoboranes with substituents of large magnetic anisotropy, such as cyclopropyl and vinyl, were to be studied to see if the range of substituents which cause observable shift differences could be extended to include these substituents.

By studying aminoboranes with functional groups, it was hoped that the effect of the substituent could be related to the nature of the N-B bond. Of particular interest were groups, such as phenyl, vinyl, chloro, which could conjugate with the N-B linkage, and thus affect the barrier to rotation. It was hoped that the chemical shifts of the substituents could be related with the barrier to rotation about the N-B bond.

The effect of a basic and an acidic solvent on the barrier to restricted rotation about the N-B bond was to be studied. A careful proton chemical shift study of the substituent groups was planned. The effect of both temperature and solvents on the shifts was to be investigated. Changes of shift with temperature or solvent might indicate changes in the bonding of the aminoborane.

The aminoboranes with vinyl on the boron are examples of compounds of the type N=B-C=C, which can be considered semi-analogs of the butadiene system. Compounds of this type have previously not been described. It was hoped that the present NMR investigation would furnish information on the effect of the vinyl group on the N-B bond. Whether conjugation over the entire system is great enough to restrict the rotation about the B-C vinyl bond remains to be seen.

The careful determination of the B^{11} shifts of a number of aminoboranes and related nitrogen-boron compounds was planned in order to obtain correlation between the boron shifts and the substituent effects.

EXPERIMENTAL TECHNIQUE

The nuclear magnetic resonance spectra were obtained on a Varian model DP-60 spectrometer. The proton spectra were run at 60 Mc operating frequency, while the boron resonances were obtained at 19.3 Mc.

The sample temperature was $+(32 \pm 2)$°C, unless otherwise specified. For temperature dependence runs the Varian variable temperature probe was employed. The temperature of the sample was changed by passing a stream of cooled or heated nitrogen past the sample. Once a desired temperature was reached, the sample was equilibrated at least one-half hour before measurements were begun. The temperature during a given run was held constant to ± 1°C. The sample temperature was monitored with a copper-constantan thermocouple. The thermocouple and the probe had previously been calibrated using the known temperature dependence of the chemical shifts of methanol and of ethylene glycol. The temperatures reported are believed to be accurate to ± 2°C.

The samples of $C_6H_{11}(CH_3)N\text{-}B(CH_3)_2$, $C_6H_5(CH_3)N\text{-}B(CH_3)_2$, $C_6H_{11}(CH_3)N\text{-}B(Cl)_2$, $(C_2H_5)_2N\text{-}B(Cl)_2$, and $C_6H_5(C_2H_5)N\text{-}B(Cl)_2$ were prepared by Dr. G. E. Ryschkewitsch, of this department. All the other samples were supplied by Dr. K. Niedenzu and Dr. P. Fritz of Durham, North Carolina.

Solutions of the samples were prepared in a DriLab Vacuum Atmospheres, Inc., dry-box. Only solvents thoroughly dried over molecular sieve were used. The neat liquid samples or the solutions were then degassed and sealed under vacuum.

The lower temperature limit of the investigations was set by the freezing point or the loss of resolution of the given sample. The upper temperature limit was set by the vapor pressure of the sample that was deemed safe for a sealed sample tube. Thus a sample was not heated beyond approximately 10° below its boiling point at atmospheric pressure.

The spectra were calibrated using audio frequency modulation. The sweep rate was found to be linear to better than 3 per cent. All the values reported for the chemical shifts and the peak separations are the average of five to ten independent determinations, unless otherwise noted. The indicated scatter in these values is the average deviation from the mean of these determinations.

EXPERIMENTAL RESULTS

The Proton Spectra

The peaks in the proton spectra of all the aminoboranes in this study could be assigned without difficulty. The spectra of these aminoboranes agree well in appearance, chemical shift, fine-structure and area ratio with those of aminoboranes to be found in the literature. No aminoboranes with vinyl on boron or cyclopropyl on nitrogen have been reported in the literature, but the assignment of these substituents in the present compounds could be made by analogy with their assignments in other organic compounds.

The samples of the present study were pure except for a small impurity peak, area ratio corresponding to 0.1 hydrogen or less, just up-field of the NCH_3 peak in $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ and $(CH_3)_2N\text{-}B(CH_3)Cl$. The sample of $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$ contained two of these small peaks.

The sample of $C_3H_5(H)N\text{-}B(CH_3)_2$ contained three small impurity peaks, area ratios less than 0.1 hydrogen, at 6.3, 6.5, and 7.1 τ. These small impurity peaks had been present in the spectra of the amines which were used as the starting material (23).

The sample of $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$ contained a small amount of vinylic polymer. At elevated temperatures the vinylic polymer became visible as a broad peak at 8.4 τ.

All the samples, except $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$ and $(CH_3)_2N\text{-}B(CH_3)Cl$ were liquids at room temperature. For the liquid samples, the temperature dependence of the non-equivalent groups was first investigated in the neat liquid sample. Usually the temperature range for a neat liquid aminoborane was considerably greater than for a CCl_4 solution of the same compound. The results of the neat liquid investigations are to be found in Tables 1, 5, 6, 7, and 19.

To minimize possible solute-solute interactions, chemical shifts are best determined in dilute CCl_4 solutions. The temperature dependences of the chemical shifts and of the non-equivalent peak separations have been investigated in CCl_4 solutions for all the samples except $C_3H_5(H)N\text{-}B(CH_3)_2$, for which the sample had to be saved for dilution studies in other solvents. The results of the CCl_4 studies are summarized in Tables 8, 9, 10, 11, 20, and 21.

Since the chemical shifts showed such small temperature dependence, whenever possible the shifts have been determined and reported to 0.001 ppm, although, in many cases, the experimental scatter was a good bit larger than 0.001 ppm. As was mentioned in the section on the experimental technique, the experimental scatter is the average deviation from the mean of five to ten independent determinations. Only by determining and reporting the chemical shifts to an extra significant figure could we hope to establish the presence of any weak temperature dependence of the chemical shifts.

In the aminoboranes of this study, the phenyl spectrum usually consists of a large central peak and several small lines. In reporting the chemical shift, the position of the large peak was given. No attempt has been made to analyze the spectrum of the phenyl group further.

Computer analysis of the spectrum of the vinyl group is planned. Until such an analysis is complete, the chemical shifts of the individual protons in the vinyl group cannot be determined. In the tabulations of the chemical shifts the position of a prominent central peak in the vinyl part of the spectrum has been included.

No attempt has been made to analyze the spectra of the n-C_4H_9 and C_3H_5 groups, and estimates as to their chemical shifts are generally not included in the chemical shift tables.

The temperature dependences were investigated in the mildly acidic solvent, $CDCl_3$, for $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$, n-$C_4H_9(CH_3)N\text{-}B(C_6H_5)CH{=}CH_2$, and $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$. The results of these investigations are to be found in Tables 14, 16, 17, and 22.

The room temperature spectrum of neat liquid $C_3H_5(H)N\text{-}B(CH_3)_2$ consists of a broad NH peak at 7.4 τ, a group of seven unsymmetrical lines centered at 7.55 τ, attributed to the CH proton, and finally a complex group of lines above 9 τ, belonging to the CH_2 and BCH_3 protons. Since the CH_2 and BCH_3 resonances overlap to a considerable extent, solvent studies in benzene and m-xylene have been carried out to achieve preferential shielding and separation of these peaks. The results of these studies are contained in Tables 2, 3, and 4.

The results of the studies in d_6-DMS as solvent are summarized in Tables 13, 15, and 18. For the d_6-DMS solutions the d_5-DMS peak of the solvent had to be used as the standard, since TMS is insoluble in this solvent. The chemical shift of the d_5-DMS peak in a 1:1 $CDCl_3$ solution with TMS internal standard has been found to be $7.458 \pm .007$ τ. In all the other solvents and in neat $C_3H_5(H)N\text{-}B(CH_3)_2$ TMS internal has been used as the standard.

Unless specifically otherwise stated, the aminoboranes were not decomposed by the solvents used. In particular d_6-DMS did not decompose $C_3H_5(H)N\text{-}B(CH_3)_2$, $(CH_3)_2N\text{-}B(CH{=}CH_2)CH_3$, $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH_3$, and $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$. Except for changes in the contours of some of the non-equivalent peaks, the spectra of the aminoboranes in the solvents used were identical in appearance, fine structure and area ratio with those of the neat liquid samples or the CCl_4 solutions. The chemical shifts, except for the anticipated solvent effects, were the same also. The changes in the shapes of some of the non-equivalent peaks in the d_6-DMS solutions will be discussed later. These changes had been anticipated and they do not indicate that the sample was ruptured by d_6-DMS.

The room temperature chemical shifts and peak separations of the aminoboranes in various solutions are summarized in Table 23.

The B^{11} Resonances

The boron chemical shifts have been obtained relative to external $B(OCH_3)_3$. Liquid samples have been run neat and solids in CCl_4 solution, unless otherwise indicated. The boron shifts for the aminoboranes and for the related nitrogen-boron compounds are contained in Table 24.

TABLE 1

TEMPERATURE DEPENDENCE OF $C_3H_5(H)N\text{-}B(CH_3)_2$. NEAT LIQUID

Temperature	Chemical Shift (τ)				BCH_3 Peak
(°C)	CH(4)*	$CH_2(3)$**	BCH_3		Separation (ppm)
+50	7.53±.02	9.441±.014	9.621±.014	9.816±.014	.195±.003
+31	7.55±.02	9.467±.014	9.630±.007	9.827±.007	.197±.002
+10	7.55±.02	9.460±.008	9.632±.003	9.832±.004	.200±.002
-10	7.54±.03	9.457±.009	9.641±.003	9.836±.003	.195±.003
-31	7.57±.02	9.466±.005	9.645±.002	9.842±.002	.197±.002
-50	7.57±.02	9.449±.007	9.645±.005	9.842±.005	.197±.003
-70	7.57±.02	9.452±.007	9.642±.003	9.840±.003	.198±.003
-90	7.58±.02	9.452±.007	9.642±.002	9.837±.002	.195±.003

*Chemical shift of the 4th observable peak from down-field in the CH part of the spectrum. The position of this peak is an approximation to the chemical shift of the CH proton.

**Chemical shift of the 3rd observable peak from down-field in the CH_2 part of the spectrum.

TABLE 2

QUALITATIVE DILUTION STUDY OF $C_3H_5(H)N\text{-}B(CH_3)_2$ IN BENZENE

Approximate Volume Sample to Volume Solvent	Chemical Shifts (τ) BCH_3		BCH_3 Peak Separation (ppm)
1:1	9.544±.014	9.760±.008	.209±.005
1:3	*	*	*
1:7	9.473±.017	9.678±.008** 9.695±.0017	.205±.005** .222±.007

[*] At 1:3 dilution the BCH_3 and the CH_2 peaks overlap to such an extent that the BCH_3 peaks could not be singled out.

[**] The up-field BCH_3 peak is quite broad at this dilution due to overlap with some of the CH_2 lines. Hence the ambiguity as to the exact location of this peak in the spectrum.

TABLE 3

CONCENTRATION DEPENDENCE OF $C_3H_5(H)N\text{-}B(CH_3)CH_3$ IN m-XYLENE SOLUTIONS

Volume Sample to Volume Solvent	Chemical Shift (τ) BCH_3		BCH_3 Peak Separation (ppm)
1:1	9.586±.011	9.808±.006	.222±.007
1:3	*	*	*
1:7	9.568±.011	9.747±.010** 9.762±.008	.180±.003** .195±.002
1:15	9.575±.002	9.745±.003	.167±.005

*At 1:3 dilution the BCH_3 and the CH_2 peaks overlap to such an extent that the BCH_3 peaks could not be singled out.

**The up-field BCH_3 peak is quite broad at this dilution due to overlap with some of the CH_2 lines. Hence the ambiguity as to the exact location of this peak in the spectrum.

TABLE 4

TEMPERATURE DEPENDENCE OF $C_3H_5(H)N-B(CH_3)_2$.
SOLUTION: 1 VOLUME SAMPLE TO 15 VOLUMES m-XYLENE

Temperature (°C)	Chemical Shift (τ) BCH_3		BCH_3 Peak Separation (ppm)
+60	9.588±.010	9.758±.006	.175±.008
+44	9.580±.014	9.752±.010	.172±.007
+32	9.575±.002	9.745±.003	.167±.005
+ 8	9.512±.004	9.736±.004	.223±.005
-12	9.485±.008	9.723±.003	.228±.008
-34	9.491±.008	9.705±.008	.213±.007
-52	9.525±.006	9.731±.003	.207±.007

TABLE 5

TEMPERATURE DEPENDENCE OF THE NCH_3 PEAK SEPARATIONS OF $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$. NEAT LIQUID

Temperature (°C)	NCH_3 Peak Separation (ppm)
+70	.047 ± .002
+50	.048 ± .003
+32	.047 ± .002
+12	.052 ± .002
- 8	.053 ± .002
-34	.053 ± .003
-50	.053 ± .003
-70	.062 ± .007
-90	.063 ± .003

TABLE 6

TEMPERATURE DEPENDENCE OF THE NCH_3 PEAK SEPARATION OF $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$. NEAT LIQUID

Temperature (°C)	NCH_3 Peak Separation (ppm)
+120	.217 ± .005
+ 90	.207 ± .005
+ 59	.205 ± .005
+ 32	.198 ± .005
+ 10	.195 ± .003
- 10	.187 ± .003

TABLE 7

TEMPERATURE DEPENDENCE OF THE NCH_3 PEAK SEPARATION OF $n\text{-}C_4H_9(CH_3)N\text{-}B(C_6H_5)CH{=}CH_2$. NEAT LIQUID

Temperature (°C)	NCH_3 Peak Separation (ppm)
+120	.225 ± .003
+ 90	.220 ± .005
+ 59	.213 ± .005
+ 32	.207 ± .005
+ 10	.204 ± .002
- 10	.198 ± .003

TABLE 8

TEMPERATURE DEPENDENCE OF $(CH_3)_2N-B(CH_3)CH=CH_2$.
SOLUTION: 1 VOLUME SAMPLE TO 2 VOLUMES CCl_4

Temperature	Chemical Shifts (τ)				NCH_3 Peak Separation (ppm)
(°C)	$CH=CH_2$*	NCH_3		BCH_3	
+71	3.89±.03	7.20±.02	7.24±.02	9.68±.01	.045±.003
+50	3.89±.04	7.21±.02	7.25±.02	9.66±.01	.045±.003
+32	3.91±.01	7.19±.01	7.23±.01	9.68±.01	.045±.003
+10	3.89±.01	7.18±.01	7.22±.01	9.67±.01	.045±.003
-10	3.89±.01	7.17±.01	7.21±.01	9.67±.01	.042±.003

*Chemical shift of the 5th observable peak from down-field in the vinyl part of the spectrum.

TABLE 9

TEMPERATURE DEPENDENCE OF $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$. SOLUTION: DILUTE IN CCl_4

Temperature	Chemical Shifts (τ)				NCH_3 Peak Separation (ppm)
(°C)	C_6H_5	$CH{=}CH_2$*	NCH_3		
+70	2.760±.027	3.749±.031	7.039±.024	7.264±.024	.235±.007
+50	2.811±.004	3.758±.003	7.067±.005	7.302±.005	.235±.002
+32	2.813±.005	3.757±.009	7.058±.006	7.286±.006	.229±.002
+10	2.789±.026	3.734±.050	7.058±.015	7.288±.015	.230±.003**
- 6	2.813±.015	3.726±.030	7.085±.015	7.350±.015	.227±.002

*Chemical shift of the 4th observable peak from down-field in the vinyl part of the spectrum.

**Average of only four independent determinations.

TABLE 10

TEMPERATURE DEPENDENCE OF n-$C_4H_9(CH_3)N-B(C_6H_5)CH=CH_2$. SOLUTION: 1 VOLUME SAMPLE TO 2 VOLUMES CCl_4

Temperature	Chemical Shifts (τ)				NCH_3 Peak Separation
(°C)	C_6H_5	$CH=CH_2$*	NCH_3		(ppm)
+70	2.825±.008	3.752±.027	7.091±.014	7.322±.014	.232±.005
+51	2.814±.006	3.730±.014	7.070±.017	7.303±.017	.233±.005
+32	2.789±.014	3.717±.014	7.052±.014	7.282±.014	.230±.007
+ 9	2.816±.012	3.735±.010	7.084±.014	7.317±.014	.233±.007
-10	2.805±.021	3.722±.052**	7.081±.018**	7.311±.018**	.230±.002

* Chemical shift of the 4th observable peak from down-field in the vinyl part of the spectrum.

** Average of only four independent determinations.

TABLE 11

TEMPERATURE DEPENDENCE OF THE PROTON CHEMICAL SHIFTS OF $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$. SOLUTION: SATURATED IN CCl_4

Temperature	Chemical Shift (τ)		
(°C)	C_6H_5*	$CH{=}CH_2$**	NCH_3
+70	2.94 ± .01	4.17 ± .01	6.92 ± .01
+50	2.95 ± .01	4.16 ± .05	6.91 ± .01
+32	2.93 ± .01	4.21 ± .03	6.91 ± .01
+10	2.90 ± .01	4.20 ± .06	6.93 ± .01
0	2.88 ± .01	4.21 ± .01	6.93 ± .01
-10	2.88 ± .01	4.20 ± .01	6.92 ± .01
-20	2.88 ± .01	4.21 ± .01	6.92 ± .01

*Chemical shift of the tallest peak in the phenyl part of the spectrum.

**Chemical shift of the 7th peak from upfield in the vinyl part of the spectrum. The position of this peak is an approximation of the average chemical shift of the strongly collapsed vinyl part of the spectrum.

TABLE 12

TEMPERATURE DEPENDENCE OF THE NCH_3 PEAK WIDTH OF $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$. SOLUTION: SATURATED IN CCl_4

Temperature (°C)	Full Width at Half Maximum Intensity (cps)
+70	1.5 ± .1
+61	2.0 ± .2
+50	2.2 ± .1
+41	3.3 ± .2
+37	3.5 ± .2
+34	3.5 ± .2
+32	4.5 ± .2
+20	5.6 ± .3
+10	4.4 ± .2
0	3.1 ± .3
-10	2.0 ± .1
-20	2.8 ± .3

TABLE 13

COMPARISON OF PROTON CHEMICAL SHIFTS AND NCH_3 PEAK WIDTHS IN VARIOUS SOLUTIONS OF $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH\text{=}CH_2$

Solution	Chemical Shifts (τ)*			Full Width at Half Maximum Intensity of NCH_3 Peak (cps)
	C_6H_5	$CH\text{=}CH_2$**	NCH_3	
Saturated solution in CCl_4	$2.93 \pm .01$	$4.21 \pm .03$	$6.91 \pm .01$	$4.5 \pm .2$
1 Volume saturated CCl_4 solution to 3 volumes CCl_4	$2.87 \pm .01$	$4.21 \pm .02$	$6.86 \pm .01$	$4.7 \pm .2$
1 Volume saturated CCl_4 solution to 1 volume d_6-DMS	$2.84 \pm .02$*** $2.94 \pm .02$	$4.15 \pm .02$	$7.01 \pm .02$	$1.3 \pm .1$

---

*Solvent peak as reference ($\tau = 7.46 \pm .01$) for the d_6-DMS solution; TMS internal reference for the CCl_4 solutions.

**Chemical shift of the 7th peak from up-field in the vinyl part of the spectrum.

***In this solution the phenyl part of the spectrum consists of two broad peaks of equal intensity.

TABLE 14

TEMPERATURE DEPENDENCE OF $(CH_3)_2N\text{-}B(CH_3)CH\text{=}CH_2$.
SOLUTION: 1 VOLUME SAMPLE TO 1 VOLUME $CDCl_3$

Temperature	Chemical Shifts (τ)				NCH_3 Peak
(°C)	$CH\text{=}CH_2$*	NCH_3		BCH_3	Separation (ppm)
32	3.827±.004	7.193±.006	7.245±.006	9.647±.005	.052±.001
0	3.833±.009	7.193±.006	7.246±.006	9.645±.004	.053±.001
-62	3.801±.007	7.201±.004	7.259±.004	9.651±.006	.058±.001

*Chemical shift of the 5th observable peak from down-field in the vinyl part of the spectrum.

TABLE 15

PROTON CHEMICAL SHIFTS AND NCH_3 PEAK SEPARATION AT 32°C OF $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$. SOLUTION: SATURATED IN d_6-DMS

Chemical Shifts (τ)*				NCH_3 Peak Separation (ppm)
$CH{=}CH_2$**	NCH_3		BCH_3	
3.81±.02	7.21±.01	7.25±.01	9.68±.02	.048±.002

*The d_5-DMS peak of the solvent was used as reference. The value of this peak was taken as 7.46±.01.

**Chemical shift of the 5th observable peak from down-field in the vinyl part of the spectrum.

TABLE 16

TEMPERATURE DEPENDENCE OF $(CH_3)_2N-B(C_6H_5)CH=CH_2$.
SOLUTION: 1 VOLUME SAMPLE TO 3 VOLUMES $CDCl_3$

Temperature	Chemical Shifts (τ)				NCH_3 Peak Separation
(°C)	C_6H_5	$CH=CH_2$*	NCH_3		(ppm)
+34	2.765±.013	3.707±.018	7.079±.026	7.317±.014	.238±.003
-10	2.718±.010	3.665±.016	7.055±.016	7.293±.014	.238±.005
-50	2.678±.009	3.624±.036	7.043±.014	7.269±.014	.227±.005

*Chemical shift of the 4th observable peak from down-field in the vinyl part of the spectrum.

TABLE 17

TEMPERATURE DEPENDENCE OF n-$C_4H_9(CH_3)N-B(C_6H_5)CH=CH_2$. SOLUTION: 1 VOLUME SAMPLE TO 1 VOLUME $CDCl_3$

Temperature	Chemical Shifts (τ)				NCH_3 Peak
(°C)	C_6H_5	$CH=CH_2$*	NCH_3		Separation (ppm)
+32	2.677±.013	3.554±.023	7.044±.016	7.271±.016	.227±.005
- 2	2.764±.029	3.661±.009	7.118±.029	7.341±.029	.223±.002
-47	2.770±.014	3.683±.020	7.142±.013	7.355±.013	.213±.003

*Chemical shift of the 4th observable peak from down-field in the vinyl part of the spectrum.

TABLE 18

CHEMICAL SHIFTS AND NCH_3 PEAK SEPARATION OF $n-C_4H_9(CH_3)N-B(C_6H_5)CH=CH_2$.
SOLUTION: SATURATED IN d_6-DMS

Chemical Shifts (τ)				NCH_3 Peak Separation (ppm)
C_6H_5	$CH=CH_2$*	NCH_3		
2.719±.004	3.509±.010	7.046±.001	7.306±.001	.260±.005

*Chemical shift of the 4th observable peak from down-field in the vinyl part of the spectrum.

TABLE 19

TEMPERATURE DEPENDENCE OF THE NCH_3 PEAK SEPARATION OF $(CH_3)_2N\text{-}B(Cl)C_4H_9$. NEAT LIQUID

Temperature (°C)	NCH_3 Peak Separation (ppm)
+78	.063 ± .001
+68	.061 ± .002
+60	.061 ± .001
+52	.061 ± .002
+43	.062 ± .001
+32	.065 ± .001
+ 8	.064 ± .002
- 6	.065 ± .002
-22	.066 ± .002
-34	.064 ± .001
-50	.069 ± .004
-70	.066 ± .003
-90	.070 ± .001

TABLE 20

TEMPERATURE DEPENDENCE OF $(CH_3)_2N-B(Cl)CH_3$.
SOLUTION: SATURATED IN CCl_4

Temperature (°C)	Chemical Shifts (τ) NCH$_3$		Chemical Shifts (τ) BCH$_3$	NCH$_3$ Peak Separation (ppm)
+60	7.122±.007	7.184±.007	9.416±.028	.063±.002
+41	7.114±.008	7.174±.007	9.411±.015	.060±.007
+32	7.115±.007	7.175±.007	9.414±.010	.060±.002
+20	7.110±.014*	7.167±.014*	9.390±.007*	.057±.002
0	7.104±.006	7.160±.006	9.410±.003	.057±.005
-20	7.117±.006	7.168±.006	9.410±.014	.051±.010

*Result of only three independent determinations.

TABLE 21

TEMPERATURE DEPENDENCE OF $(CH_3)_2N-B(Cl)n-C_4H_9$. SOLUTION:1 VOLUME SAMPLE TO 2 VOLUMES CCl_4

Temperature (°C)	Chemical Shift (τ) NCH_3		NCH_3 Peak Separation (ppm)
+70	7.011±.002	7.072±.002	.061±.002
+51	6.926±.005	6.983±.005	.057±.001
+34	6.908±.015	6.967±.015	.059±.001
+10	6.952±.008	7.008±.008	.056±.001
-11	6.925±.007	6.979±.007	.054±.002

TABLE 22

TEMPERATURE DEPENDENCE OF $(CH_3)_2N-B(Cl)n-C_4H_9$. SOLUTION: 1 VOLUME SAMPLE TO 1 VOLUME $CDCl_3$

Temperature (°C)	Chemical Shift (τ) NCH_3		NCH_3 Peak Separation (ppm)
+34	6.933±.014	7.000±.014	.067±.001
-10	6.949±.012	7.014±.012	.065±.003
-50	6.946±.013	7.012±.013	.066±.002

TABLE 23

CHEMICAL SHIFTS AND PEAK SEPARATIONS OF THE AMINOBORANES IN VARIOUS SOLUTIONS

Compound and Solution	C_6H_5 τ	CH=CH_2 τ	NCH_3 τ		NCH_3 Peak Separation (ppm)	BCH_3 τ	BCH_3 Peak Separation (ppm)
$(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ neat	-	-	-	-	.047±.002	-	-
1 volume sample to 2 volumes CCl_4	-	3.91±.01^a	7.19±.01	7.23±.01	.045±.003	9.68±.01	-
1 volume sample to 1 volume $CDCl_3$	-	3.827±.004^a	7.193±.006	7.245±.006	.052±.001	9.647±.005	-
saturated in d_6-DMS	-	3.81±.02^a	7.20±.01	7.25±.01	.048±.002	9.68±.02	-
$(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$ neat	-	-	-	-	.198±.005	-	-
dilute in CCl_4	2.813±.005	3.757±.009^b	7.058±.006	7.286±.006	.228±.002	-	-
1 volume sample to 3 volumes $CDCl_3$	2.765±.013	3.707±.018^b	7.079±.026	7.314±.026	.235±.003	-	-
$n\text{-}C_4H_9(CH_3)N\text{-}B(C_6H_5)CH{=}CH_2$ neat	-	-	-	-	.212±.005	-	-
1 volume sample to 2 volumes CCl_4	2.789±.002	3.717±.012^b	7.052±.014	7.282±.014	.230±.007	-	-
1 volume sample to 1 volume $CDCl_3$	2.677±.013	3.554±.023^b	7.044±.016	7.271±.016	.227±.005	-	-
saturated in d_6-DMS	2.719±.004	3.509±.010^b	7.046±.001	7.306±.001	.260±.005	-	-
$(CH_3)_2N\text{-}B(CH_3)Cl$ saturated in CCl_4	-	-	7.115±.007	7.175±.007	.060±.002	9.414±.010	-
$(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$ neat	-	-	-	-	.065±.002	-	-
1 volume sample to 2 volumes CCl_4	-	-	6.908±.015	6.967±.015	.059±.005	-	-
1 volume sample to 1 volume $CDCl_3$	-	-	6.933±.014	7.000±.014	.067±.004	-	-

Table 23 (cont'd)

$CH_3(C_6H_5)N$-$B(C_6H_5)CH$=CH_2 saturated in CCl_4	2.93±.01	4.21±.03[c]	6.91±.01		-	-		-
1 volume saturated in CCl_4 to 3 volumes CCl_4	2.87±.01	4.21±.02[c]	6.86±.01		-	-		-
1 volume saturated in CCl_4 to 1 volume d_6-DMS	2.94±.02 2.84±.01	4.15±.02[c]	7.01±.02		-	-		-
$C_3H_5(n)N$-$B(CH_3)_2$ neat	-	-	-	-	-	9.630±.007	9.827±.007	.197±.002
1 volume sample to 1 volume C_6H_6	-	-	-	-	-	9.544±.014	9.760±.008	.208±.005
1 volume sample to 7 volumes C_6H_6	-	-	-	-	-	9.473±.017	9.695±.017	.205±.008
1 volume sample to 1 volume m-$C_6H_5CH_3$	-	-	-	-	-	9.586±.011	9.808±.006	.222±.007
1 volume sample to 7 volumes m-$C_6H_5CH_3$	-	-	-	-	-	9.568±.008	9.747±.010[d] 9.762±.008[d]	.180±.003[d] .195±.003[d]
1 volume sample to 15 volumes m-$C_6H_5CH_3$	-	-	-	-	-	9.575±.002	9.745±.002	.167±.005

[a] Chemical shift of the 5th observable peak from down-field in the CH=CH_2 part of the spectrum.

[b] Chemical shift of the 4th observable peak from down-field in the CH=CH_2 part of the spectrum.

[c] Chemical shift of the 7th peak from up-field in the CH=CH_2 part of the spectrum.

[d] Alternate peak assignments.

TABLE 24

B^{11} CHEMICAL SHIFTS OF SOME AMINOBORANES

Entry	Formula	Chemical Shift (ppm from $B(OCH_3)_3$)	
1	$C_6H_{11}(CH_3)N-B(CH_3)CH_3$	$-26.3 \pm .06$	$-27.6 \pm .9$
2	$C_3H_5(H)N-B(CH_3)CH_3$	$-28.8 \pm .04$	
3	$C_6H_5(CH_3)N-B(CH_3)CH_3$	$-27.8 \pm .2$	
4	$C_6H_5(CH_3)N-B(CH_3)C_6H_5$	$-26.3 \pm .1$	
5	$CH_3(CH_3)N-B(CH_3)CH=CH_2$	$-21.4 \pm .05$	
6	$CH_3(CH_3)N-B(C_6H_5)CH=CH_2$	$-21.9 \pm .2$	$-21.3 \pm .5$
7	$CH_3(n-C_4H_9)N-B(C_6H_5)CH=CH_2$	$-20.8 \pm .1$	
8	$CH_3(CH_3)N-B(Cl)n-C_4H_9$	$-20.7 \pm .03$	
9	$C_6H_{11}(CH_3)N-B(Cl)Cl$	$-12.0 \pm .2$	$-12.2 \pm .3$
10	$C_2H_5(C_2H_5)N-B(Cl)Cl$	$-12.0 \pm .05$	
11	$C_6H_5(CH_3)N-B(Cl)Cl$	$-12.7 \pm .1$	
12	$CH_3(CH_3)N-B\ CH_3$ $CH_3(CH_3)N-B\ CH_3$	$-32.2 \pm .05$	

Table 24 (Cont'd)

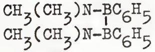
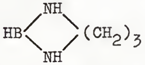
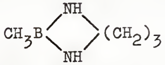
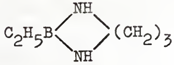
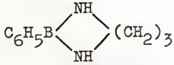
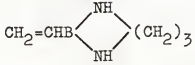
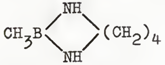
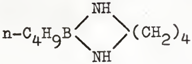
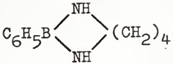
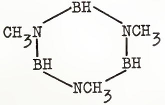
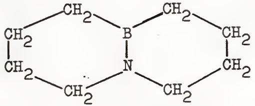
Entry	Formula	Chemical Shift (ppm from $B(OCH_3)_3$)
13	 $CH_3(CH_3)N-BC_6H_5$ $CH_3(CH_3)N-BC_6H_5$	-27.3±.1
14		- 7.1±.4
15		-11.8±.1
16		-12.0±.02
17		- 9.0±.01
18		- 8.9±.1

Table 24 (Cont'd)

Entry	Formula	Chemical Shift (ppm from $B(OCH_3)_3$)
19	 *	$-11.8\pm.1$
20	 *	$-12.5\pm.1$
21	 *	$-10.4\pm.05$
22		$-14.0\pm.2$
23	 *	$-3.8\pm.02$

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*Benzene solution of the sample.

DISCUSSION OF RESULTS

The Proton Spectra

Compounds of the type YY'N-BRR'.-One representative of this type of compound, $C_3H_5(H)N\text{-}B(CH_3)_2$, has been investigated. The room temperature spectrum of this compound has already been discussed in the section on experimental results.

As the temperature of the sample was lowered, its NMR spectrum changed markedly. Two tall, fairly broad peaks began to emerge on the up-field side of the complex of lines belonging to the CH_2 and BCH_3 protons. These two lines are attributed to the non-equivalent boron methyl groups. The author believes this is the first time non-equivalence of the boron substituents has been observed when there was no phenyl substituent on the nitrogen.

As the temperature of the sample was further lowered, the BCH_3 peaks in the spectrum sharpened up. No spectra could be obtained below -100°C, since resolution in the spectrum became too poor due to the increased viscosity of the sample. At -100°, the ratio of the up-field BCH_3 peak area to the combined area of the low-field BCH_3 and the CH_2 peaks was 3.4 to 6.6, indicating that even at this low temperature there is some overlap of the up-field BCH_3 peak and the CH_2 peaks.

The temperature dependence of the BCH_3 peak separation and of the chemical shifts in the neat liquid sample has been studied from -100° to +70°C. These results are contained in Table 1. From these results it can be said with a good degree of certainty that the separation of the BCH_3 peaks does not change below 0°C. The BCH_3 peaks become broad above 0°C amd merge with the CH_2 peaks. Thus the BCH_3 peaks above 0°C could be assigned only by comparing these high temperature spectra with those obtained below 0°. It must be emphasized that above 0° we do not necessarily measure the "true" position of the BCH_3 peaks, but rather the apparent position where they had become part of the complex of CH_2 and BCH_3 lines. Thus, it is not surprising that the measurements of the BCH_3 peak separations do not show the expected decrease above 0°C.

While the temperature dependences of the neat liquid sample show that the boron methyls are non-equivalent and that the BCH_3 peaks begin to merge above 0°, no useable quantitative measurements could be made due to the overlap with the CH_2 peaks.

Next a 1:1 benzene solution of the sample was prepared. It was hoped that preferential shielding of some of the protons of the sample by an aromatic solvent would move the CH_2 and BCH_3 peaks apart. In benzene the BCH_3 peaks do fall on the low-field side of the CH_2 peaks, but there is still considerable overlap. The BCH_3 peak separation in a 1:1 benzene solution agrees with that obtained for the neat liquid sample. The BCH_3 peak separation in the benzene solution remains constant within experimental error to -11°C, the lowest temperature that could be obtained with this solvent.

Next a qualitative dilution study in benzene was carried out with the hope that the CH_2 and BCH_3 peaks could be further separated. Increased separation of these peaks beyond the threefold dilution point was found to be negligible.

A quantitative dilution study in m-xylene was also made. The results agree with those of the benzene dilution study. Since m-xylene boils much higher than benzene, a temperature study was made of a solution containing 1 volume sample to 15 volumes m-xylene. The temperature was carried up to +100°C, but the BCH_3 peaks disappear so completely among the CH_2 peaks at temperatures above 60°, that these high-temperature spectra could not be analyzed. Apparently, even a +100° temperature is not quite high enough to cause the merged BCH_3 peaks to sharpen and appear as a single large peak on top of the CH_2 lines.

A 1:1 d_6-DMS solution of the sample was also prepared. Now the BCH_3 protons show up as a single, large, fairly sharp peak which is superimposed on the cyclopropyl CH_2 peaks. Thus d_6-DMS reduces the N-B double bond character, presumably by bond formation between the oxygen of the solvent and the boron of the sample, to such an extent that the BCH_3 peaks become equivalent. The large BCH_3 peak in the DMS solution of the sample did not broaden as the temperature was lowered. The temperature could not be carried below +10° since DMS crystals began to form at this temperature.

Figure 2 provides a comparison of the CH_2 and BCH_3 region of the spectrum of $C_3H_5(H)N\text{-}B(CH_3)_2$, as a neat liquid at -90°C and +32°C and as a solution in d_6-DMS at +32°C.

The results of the benzene and m-xylene solution studies are to be found in Tables 2, 3, and 4. While there appears to be a solvent effect on the BCH_3 peak separation, the values of the separation above 0° are not very certain due to peak overlap. Therefore, nothing definite can be said about the solvent effect.

While no measurements could be made which would allow one to calculate the activation energy of hindered rotation in this compound, the non-equivalence of the boron methyls has been established both from the temperature dependence of the spectra and also from the disappearance of the non-equivalence in DMS. It was also interesting to see that the cyclopropyl group was sufficiently anisotropic so as to cause non-equivalence of the boron methyls.

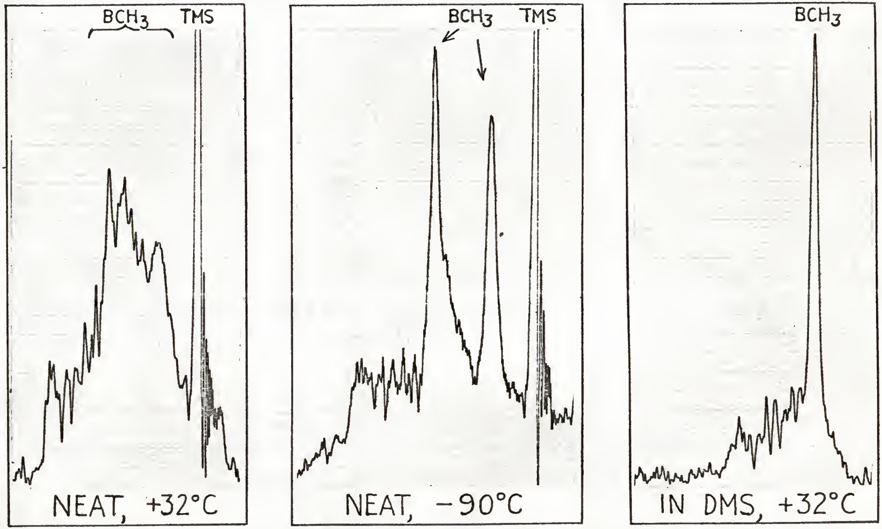

Figure 2. Comparison of the CH_2 and BCH_3 region of $C_3H_5(H)N\text{-}B(CH_3)_2$, neat and in DMS solution at +32° and -90°C.

The observed non-equivalence of the BCH_3 when a cyclopropyl group is attached to the nitrogen, is further evidence for the anisotropic character of the cyclopropyl ring. The chemical shift of 9.78 τ (24) for cyclopropyl, which is unusually high for a methylene proton, is generally attributed to the anisotropy of the cyclopropyl ring. To date, cyclopropyl has been found to be the only saturated hydrocarbon with appreciable magnetic anisotropy.

Compounds of the type RR'N-BXX'.-Five representatives of this group of compounds were investigated: $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$, $n\text{-}C_4H_9(CH_3)N\text{-}B(C_6H_5)CH{=}CH_2$, $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$ and $(CH_3)_2N\text{-}B(CH\ )Cl$.

(Dimethylamino)methylvinylborane.-The N-methyl peaks in the neat liquid spectrum of this compound show up as two separate peaks of equal intensity over the entire temperature range of the investigation (-90° to +70°C). Thus the N-methyls seem non-equivalent, although no phenyl or chlorine is attached to the boron. This is the first compound to the author's knowledge where NCH_3 non-equivalence has been observed, when no phenyl or chlorine was attached to the boron. Thus apparently the vinyl group is of sufficient magnetic anisotropy as to cause different shielding of the NCH_3 protons cis and trans to the vinyl.

The separation between the two N-methyl peaks changes very little as the temperature is raised. (See Table 5.) Such behavior is quite different from the behavior of aminoboranes that contain no vinyl on the boron.

Non-equivalence of the nitrogen substituents in aminoboranes with vinyl on the boron may arise in three ways: 1) Restricted rotation about the N-B bond could cause non-equivalence. Such restricted rotation is believed to be the cause of the magnetic non-equivalence of the substituents in aminoboranes cited in the literature. However, a high barrier to rotation seems peculiar to the boron-vinyl system.

If restricted rotation about the N-B bond is the sole cause of the non-equivalence, the raised barrier to rotation when vinyl is on the boron is contrary to expectations. One would suppose that since the vinyl group itself can form a partial double bond with the boron, there would be competition with the nitrogen-boron double bond formation, and the N-B double bond character might be decreased.

However, as Gould (25) points out in the discussion of conjugation of C≡C, one should not attach too great a physical significance to the individual canonical forms. What these forms indicate is that the atoms joined by single bonds are brought closer together by attraction between their π electrons. This "extra" attraction need not take place at the expense of the adjacent multiple bonds. Thus, while the $B\text{-}C_{vinyl}$ double bond formation does not necessarily decrease the double bond character of the N-B bond, it is not expected to increase the N-B bond order.

2) Restricted rotation about the B-C$_{vinyl}$ bond could be another source of the magnetic non-equivalence of the nitrogen substituents. Since cis-trans isomerism is possible about the B-C$_{vinyl}$ bond, it would be fortuitous if the two isomers had equal populations. The fact that the two NCH_3 peaks of $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, as well as of $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$ and $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$, have been found to be of equal area, points against restricted rotation about the B-C$_{vinyl}$ bond as the sole cause of the NCH_3 non-equivalence.

Also, if there is restricted rotation about the B-C$_{vinyl}$ bond, the vinyl protons of the two isomers are expected to be non-equivalent, though the shielding may not be very different. Only one set of peaks has been observed for the vinyl protons of $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$.

3) Finally, the nitrogen substituent non-equivalence may arise from restricted rotation about both the N-B and the B-C$_{vinyl}$ bonds. That is, there would be conjugation and restricted rotation about the bonds of the entire four atom system of the N-B-C-C grouping. For such a conjugated system one isomer is expected to be energetically favored.

Conjugation and restricted rotation throughout the four atom system with only one isomer present will account for all the observed NMR facts in $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$: NCH_3 non-equivalence and equal NCH_3 peak size; only one set of vinyl peaks; and moreover, a high barrier to rotation about the N-B bond can now be explained by the loss of conjugation throughout the four atom system that would result if there were rotation about the N-B bond. It is noteworthy, that due to conjugation a higher barrier to rotation about the N-B bond is observed, although the N-B bond may be of lower order.

Since the NCH_3 peak separation changes very little, none of the conventional methods of obtaining NMR rate constant could be employed. If the NCH_3 peak separation continues to decrease at the same rate, 0.016 ppm/100°, the peaks would merge at about +350°C. Of course, it is much more likely that the NCH_3 peaks will start to merge more rapidly and that the coalescence temperature will be considerably lower than +350°.

The spectrum of the vinyl group also changes with temperature. At the higher temperatures the =CH part of the spectrum consists of five lines: four fundamental lines and two combination lines so close together that they cannot be resolved. As the temperature is lowered, these combination lines move apart and can be resolved into two lines at about -10°C. As the temperature is further lowered, the combination lines move farther apart and lose intensity to the fundamental lines. (Compare Figures 3 and 4.)

The two $=CH_2$ protons of the vinyl group have shifts very close together, so this part of the spectrum could not be assigned by inspection. Detailed computer analysis of the vinyl spectrum will be needed to see whether the relative chemical shifts of the $=CH_2$ protons change as the =CH part of the spectrum changes. Such a parallel change in $=CH_2$ chemical shifts and combination line behavior was observed in vinyl chloride by Scott (26) as the temperature was varied and in vinyl bromide by Schaeffer and Schneider (27) as the solvent was varied.

The temperature dependence of $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ has also been investigated in CCl_4 solution with TMS as internal standard. Since the available temperature range in this solvent was only from -10° to +70°, both the NCH_3 peak separation and the chemical shifts vary very little. (See Table 8.)

The sample was also run as a saturated solution in d_6-DMS. The sample and d_6-DMS were found to be only partially miscible. The NCH_3 non-equivalence was not removed by this solvent. A possible explanation for this behavior is that since the B has a chance to form a double bond intramolecularly with the N and the vinyl C, the

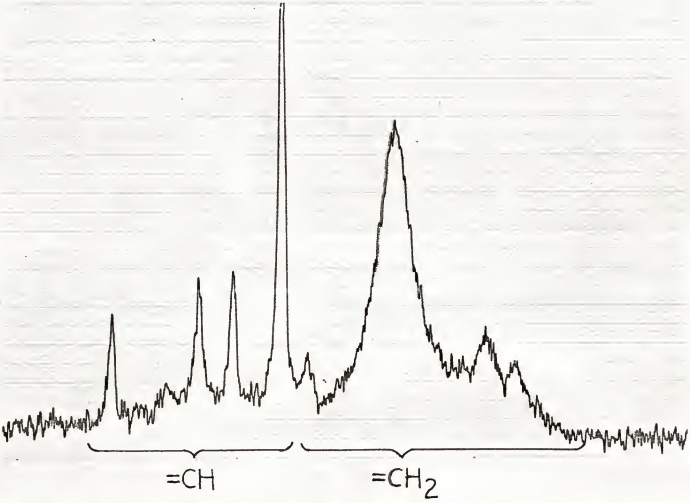

Figure 3. The vinyl part of the spectrum of neat $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ at +32°C. The third peak from the left is the superposition of the two combination lines.

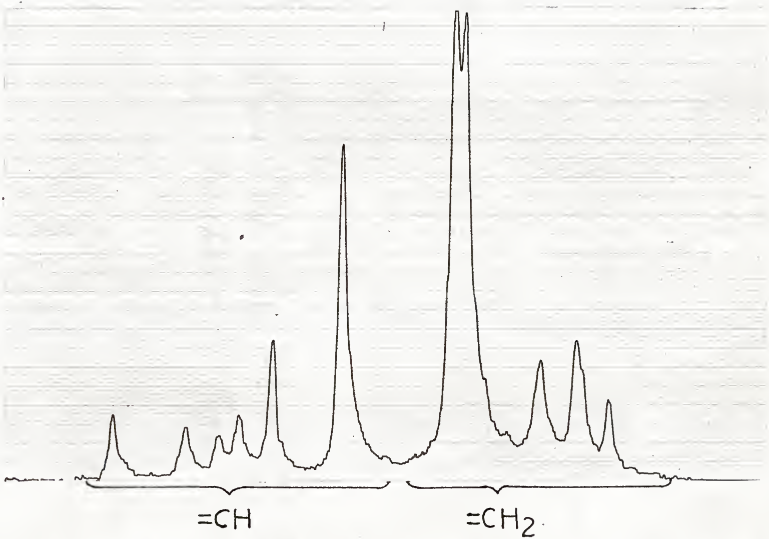

Figure 4. The vinyl part of the spectrum of neat $(CH_3)_2N{-}B(CH_3)CH{=}CH_2$ at -90°C. The third and fourth peaks from the left are the combination lines.

boron is less likely to form an acid-base pair intermolecularly with DMS.

That the DMS affects the boron very little can be seen from the B^{11} chemical shifts, which were determined both in the neat liquid and the d_6-DMS solution and were found to be identical. If there were a strong acid-base pair formation between boron and d_6-DMS, one would expect the boron to be appreciably shielded. The proton chemical shifts remain unaffected by the d_6-DMS. Again, if there were strong acid-base pair formation, the substituents on boron would be expected to be appreciably shielded, while those on the nitrogen would also be shielded, but to a lesser degree.

(Dimethylamino)phenylvinylborane and (methyl n-butylamino)phenylvinylborane.-As expected, the temperature dependences of these two compounds were very similar. The NCH_3 peaks in both compounds show up as two separate peaks over the entire temperature range from -10° to +120°C. For $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ we have seen that the vinyl group reduces the ease of rotation about the N-B bond. From the temperature dependences of these present vinylboranes, it appears that the vinyl substituent on boron stabilizes the N-B double bond, even if a phenyl is also attached to the boron. These compounds show no sign of merging or line broadening even at +120°C.

From Tables 6 and 7 we see that the NCH_3 peaks move slightly apart as the temperature is raised. Such behavior is contrary to expectation if we suppose less hindered rotation as the temperature is increased. The increased separation of the NCH_3 peaks must be due to a chemical shift change in one or both of the N-methyls.

To test if the chemical shifts of the NCH_3 change measurably, a careful study was made of the temperature dependence of the shifts. The results of the study are summarized in Tables 9 and 10. All the chemical shifts remained reasonably constant over the entire temperature range. The increase in the NCH_3 peak separation was very small, 0.03 ppm over 130°. Since the error in the chemical shift is of this magnitude or larger, the shift study could not prove our hypothesis.

Spectra have also been obtained of $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$ as a saturated solution in d_6-DMS. The sample and solvent are only partially miscible. Again, as was found for $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, this solvent did not remove the non-equivalence of the NCH_3. (See Table 18.)

(Dimethylamino)phenylvinylborane decomposes in d_6-DMS. Since none of the other aminoboranes with vinyl on the boron have been decomposed by d_6-DMS, such behavior is rather peculiar. Trace impurities may have catalyzed the decomposition.

Next a less potent reagent, $CDCl_3$, was tried. Since $CDCl_3$ is a mild acid, it was hoped that $CDCl_3$ would form an acid-base pair with the nitrogen of the aminoborane and thus remove the NCH_3 non-equivalence. While neither of the samples was decomposed in $CDCl_3$, the NCH_3 non-equivalence was neither removed nor reduced. Both the chemical shifts and the NCH_3 peak separation are the same in $CDCl_3$ as they had been in CCl_4. (Compare Table 9 with Table 16; Table 10 with Table 17.)

The vinyl spectra of $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$ and $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$, while not quite as collapsed as the vinyl spectrum of $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, still could not be analyzed by inspection. A computer analysis of the vinyl spectra and their temperature dependences is planned. The four low-field lines in the vinyl spectrum have been assigned to the $=CH$ proton, the next four lines to the $=CH_2$ proton trans to the boron, while the quartet at highest field has been assigned to the $=CH_2$ proton cis to the boron. These assignments have been made on the basis of the size of the coupling constants, the order in vinyl compounds in general being $J_{trans} > J_{cis} > J_{gem}$.

Combination lines in the $=CH$ part of the spectrum, such as have been observed for $(CH_3)_2N-B(CH_3)CH=CH_2$ do not appear in these two compounds. This is not surprising, since now the chemical shifts of the $=CH_2$ protons are farther apart. The lines belonging to the $=CH_2$ protons show broadening at high temperatures. This broadening is particularly marked for the proton trans to boron.

Comparison of Figure 5 with Figure 6 illustrates the broadening of the $=CH_2$ protons at elevated temperatures.

A Stuart-Briegleb model of the molecule was made using a sp_2 N piece for the boron and an sp_2 C piece for the nitrogen. The model indicates that the vinyl proton trans to the boron protrudes farthest from the other atoms in the molecule and should be least affected by them. However, since the exact spatial relationship between this proton and the phenyl group is not known and since the effect of the phenyl ring falls off moderately rapidly [about 90 per cent decrease in shielding over a distance of 4 Å (20)], the effect of the phenyl ring current may well be felt at the proton trans to the boron and thus aid in its relaxation and broadening. That the presence of the phenyl group on boron is rather important for the observation of such broadening, can be seen from the fact that broadening was not observed in $(CH_3)_2N-B(CH_3)CH=CH_2$.

Intermolecular interactions between the proton trans to the boron and the phenyl group on the neighboring molecule

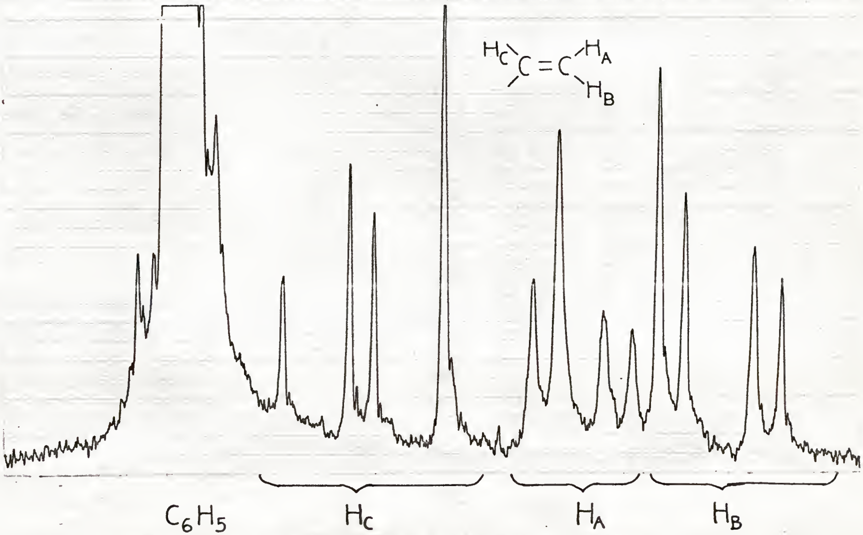

Figure 5. The phenyl and vinyl regions of neat $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$ at +32°C.

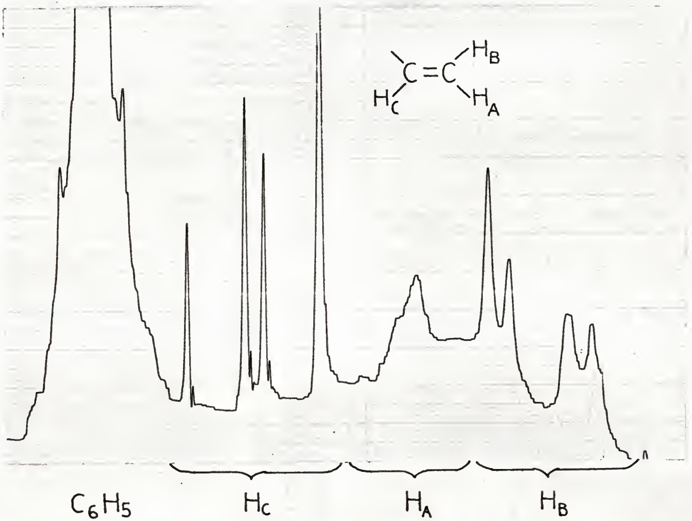

Figure 6. The phenyl and vinyl regions of neat $(CH_3)_2N-B(C_6H_5)CH=CH_2$ at +120°C.

could also account for the observed broadening. Since the proton trans to the boron protrudes frathest from the rest of the molecule, such intermolecular interactions would be most likely to affect it. Since about the same degree of broadening was observed in the CCl_4 solutions as in the neat liquid sample, the proposed intermolecular interaction would have to be a rather strong one. Also, since the broadening appears at elevated temperatures where intermolecular interactions are expected to be diminishing, intermolecular interactions appear to be the least likely explanation for the observed broadening.

Electronic changes, in particular changes in the π-electron distribution of the molecule, can affect the relaxation time and the broadening. In the vinylic system the values of J_{trans} and of the chemical shifts are good indicators of such changes (28). Therefore, a computer analysis of the temperature dependence of the vinyl groups will be most interesting. Indeed, should the computer analysis show that the line spacings are not fair indicators of the coupling constants, the line assignment may have to be changed. That is, the broadened line may not belong to the trans proton, but rather to the proton cis or gem to the boron. Since the boron vinyl spectra are strongly second order, there is a finite possibility of poor line spacing-coupling constant correspondence. Still, the same arguments as have been used for the trans proton, would also explain the broadening of the cis or gem protons. Intramolecular interactions between the proton in question and the phenyl group would be more likely for the cis or gem case than for the trans case.

The vinyl spectrum of $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$ in $CDCl_3$ and CCl_4 solutions exhibits a further unexpected feature: the resonances belonging to the $=CH$ proton and the $=CH_2$ proton cis to the boron are doubled by about 1 cps. Since the resonance lines belonging to the $=CH_2$ proton trans to the boron are broad, no splitting could be observed there. Since there is no nearby single spin-one-half nucleus to which the vinyl protons could couple, spin-spin coupling has to be ruled out as the source of the doubling. Such doubling could be due to either two non-equivalent vinyl groups or to second-order splitting. Both of these quantities are field dependent; therefore, running the proton spectrum at a different operating frequency would not give us further information. Again, computer analysis may yield the observed second-order splitting.

Two non-equivalent vinyl groups may arise in several ways: hindered rotation about the N-B bond, hindered rotation about the $B\text{-}C_{vinyl}$ bond, solvated and unsolvated solute molecules. Since the splitting was found to be the same in both the 1 volume sample to 1 volume $CDCl_3$ solution and the 1 volume sample to 2 volumes CCl_4 solution, it is rather unlikely that there would be the same fraction of solvated solute molecules with the same shielding in the two solutions.

This leaves us hindered rotation about a B bond as the source of the doubling. For the symmetrically substituted compound $(CH_3)_2N-B(C_6H_5)CH=CH_2$, there was no splitting of the vinyl peaks. This would lead one to suspect cis-trans isomerism about the N-B bond to be the cause of the vinyl splitting for the unsymmetrically substituted compound $CH_3(n-C_4H_9)N-B(C_6H_5)CH=CH_2$. However, it would be most surprising to find sufficient magnetic anisotropy between methyl and n-butyl to account for the observed vinyl splitting.

The bulkier n-butyl group may affect the bonding of the molecule, particularly the phenyl skew-angle, in such a way as to raise the barrier to rotation about the $B-C_{vinyl}$ bond. Then the vinyl splitting would be due to cis-trans isomerism about the $B-C_{vinyl}$ bond. Thus NMR alone cannot distinguish whether the rotation about the N-B or the $B-C_{vinyl}$ bond is responsible for the non-equivalence of the vinyl peaks.

Comparison of Figure 7 with Figure 8 shows the splitting of the vinyl protons gem and cis to the boron in the CCl_4 solution of the sample.

(Dimethylamino)n-butylchloroborane and (dimethylamino)methylchloroborane.-Non-equivalence of the NCH_3 protons was observed in both of these compounds.

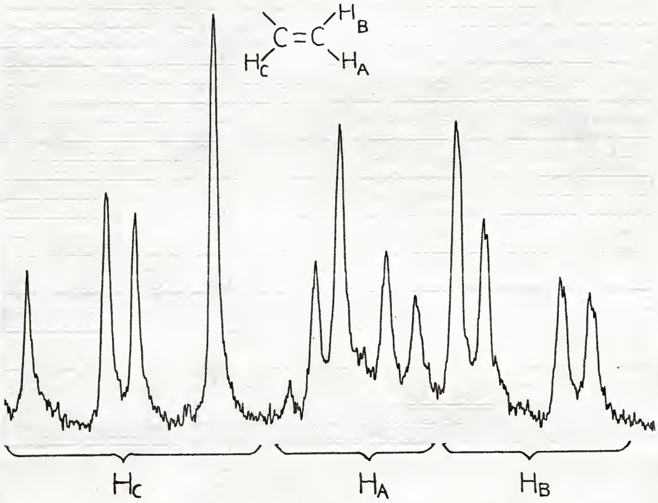

Figure 7. The vinyl part of the spectrum of neat $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$ at 32°C.

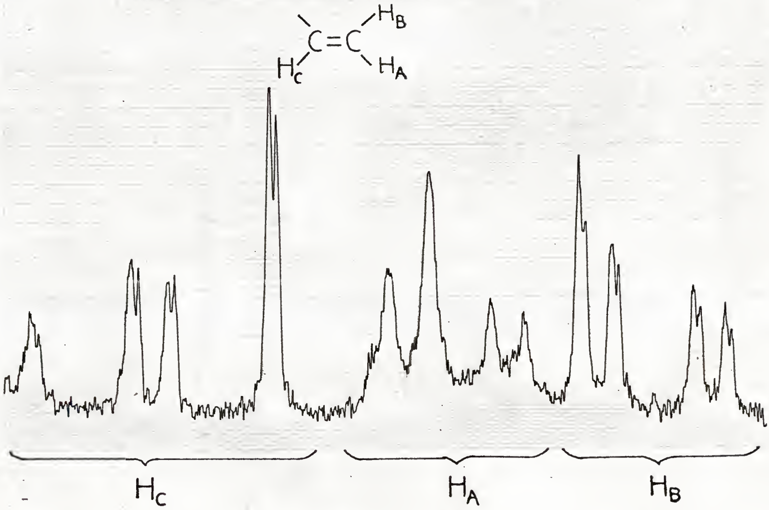

Figure 8. The vinyl part of the spectrum of $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$ in CCl_4 solution at 32°C.

The chlorine on boron is supposed to stabilize the N-B double bond according to the IR results of Becher and of Baechle (9,17). This seems to be confirmed by our NMR results: the NCH_3 peak separation in both of these compounds changes very little over the entire temperature range. In the case of chlorine, conjugation cannot be proposed as the cause of the greater N-B bond stability. However, chlorine is more electronegative than boron, so the chlorine's inductive effect may promote and stabilize the N-B double bond formation.

(Dimethylamino)n-butylchloroborane is a liquid, so its spectrum could be run as a neat liquid. The NCH_3 peak separation decreases by only 0.07 ppm over the 110° range of the temperature study. Such minute changes are probably due to chemical shift changes of the NCH_3 protons, rather than a decrease in the barrier to rotation.

Both $(CH_3)_2N\text{-}B(CH_3)Cl$ and $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$ have also been run in CCl_4 solution. The temperature dependence of $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$ in this solvent is almost identical to those of the neat liquid. For $(CH_3)_2N\text{-}B(CH_3)Cl$ the NCH_3 peak separation increases very slightly, 0.01 ppm/80°C, as the temperature is raised. Again this change is attributed to change in the shielding of the NCH_3 protons with temperature, but because the error in the chemical shifts is of the same magnitude as the change in the NCH_3 peak separation, the shift study could not establish the source of the change in the NCH_3 peak separation.

An attempt has been made to run both samples in d_6-DMS solution, but not surprisingly both samples decompose very rapidly in this solvent. Next the less potent solvent, $CDCl_3$, was tried. While neither of the compounds decomposed in this solvent, $(CH_3)_2N-B(CH_3)Cl$ was insufficiently soluble to obtain a useable spectrum. The temperature dependence of $(CH_3)_2N-B(n-C_4H_9)Cl$ in $CDCl_3$ is almost identical with that for the CCl_4 solution.

Compounds of the type $R(C_6H_5)N-B(C_6H_5)X$.-The one representative of this type of compound was $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$. The NCH_3 and the $=CH$ peaks of this compound in the CCl_4 solution are sharp at low temperatures. As the temperature of the sample is raised, these peaks show a marked broadening around room temperature. As the temperature is further increased, the peaks sharpen again. (See Table 12.)

Figure 9 shows the well-resolved vinyl spectrum at -20°C and the broadened vinyl spectrum at +10°C.

These results have been found to be quite reproducible, and the broadening was not due to field inhomogeneity, as could be seen by the sharpness of the TMS peak. The full width at half maximum peak intensity was 1.2 cps or less for TMS at all temperatures. Neither was the broadening caused

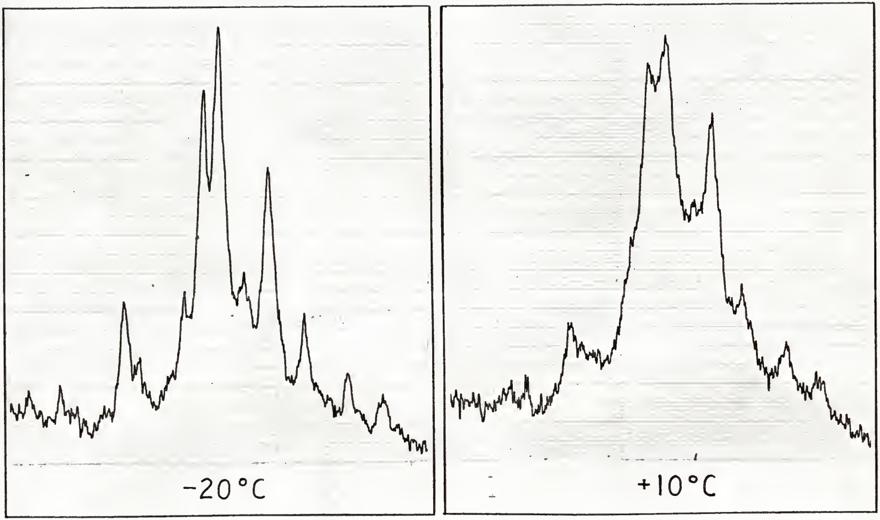

Figure 9. The vinyl part of the spectrum of $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$, saturated solution in CCl_4 at -20° and +10°C.

by dipole-dipole interaction of the solute molecules since the peak widths remained unaltered on dilution with CCl_4. (See Table 13.) This leaves interchange between magnetically non-equivalent environments as the cause of the broadening. The peak-width study in d_6-DMS (Table 13), further narrows this down to restricted rotation about a boron bond: in d_6-DMS the peaks are narrow because partial double bond character of any boron bond has been greatly reduced. Since the infra-red studies of Becher and Baechle (18) on $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH_3$ indicate that possibly restricted rotation about the B-C_{aryl} and N-C_{aryl} bonds, in addition to the N-B bond, may also be involved, we cannot say with certainty which boron bond is principally responsible for the observed NMR results. X-ray studies of $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$ are planned (29), and it is hoped that the experimental bond lengths and bond angles will shed light as to which boron bond is of highest order. The Stuart-Briegleb model of $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$ indicates that there is considerable steric hindrance to rotation about both the N-B and the B-C_{vinyl} bonds.

Thus the broadening of the NCH_3 and =CH proton peaks around room temperature may be explained by the slow interconversion between two magnetically non-equivalent states. However, the chemical shifts of these states are close enough together so that separate peaks cannot be resolved, and we only see broadening.

As the temperature is raised, interconversion between the states becomes more rapid and we see an average shift accompanied by a narrowing of lines. Thus the temperature dependence of $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$ above room temperature is analogous to the behavior of other aminoboranes above the coalescence temperature.

The narrowing of the lines below +20° can be explained by a rapid decrease in the population of the less favored isomer, so that at low temperatures we see a spectrum of essentially the favored isomer. Such a steep temperature dependence postulates a fairly large enthalpy difference between the two states. For a similar compound, $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH_3$, which also has unequal population of the two isomers at room temperature, Chakrabarty (29) has found a threefold decrease in the equilibrium constant between +55° and +20°C.

Without the simplifying assumption of equal population in the two states, the NMR rate equations have not been treated successfully as yet in the region of coalescence (30). Therefore, a quantitative analysis of the narrowing of the NCH_3 line below room temperature is not feasible. If the crude assumption is made that the populations of the two isomers are nearly equal above room temperature, the activation energy may be estimated. The further assumption was made that the rate of rotation is inversely proportional to the line width. A better estimate of the rate constant could have been made by analyzing the complete line-shape function. The extra effort did not seem justified in light of the assumption of equal population. Thus in Figure 10, the log of the inverse of the line-width, $\Delta\nu$, has been plotted against 1/T. From the slope of the plot we obtain $E_{act} = 61 \pm 6$ kcal/mole, which is very much larger than the activation energy that has been found for other aminoboranes. Considering the roughness of the approximation of equal populations, no claim can be made as to the correctness of the value of 61 kcal/mole for the activation energy.

The B^{11} Resonances

General features of the boron resonances

As expected, all the boron resonances were broad, due to the enhancement of the quadrupolar broadening by the nitrogen. The resonances for the phenyl containing compounds were particularly broad: 80 to 400 cps full width at half maximum peak intensity. Apparently the magnetic anisotropy of the phenyl ring contributes to relaxation and broadening. The widths of the boron resonances in samples containing no phenyl group ranged from 35 to 75 cps full width at half maximum peak intensity. No further generalizations could be made as to the effect of substituent or of bonding on peak width.

With the exception of the samples containing hydrogen directly on the boron, all the boron resonances were singlets. In the samples containing hydrogen directly on

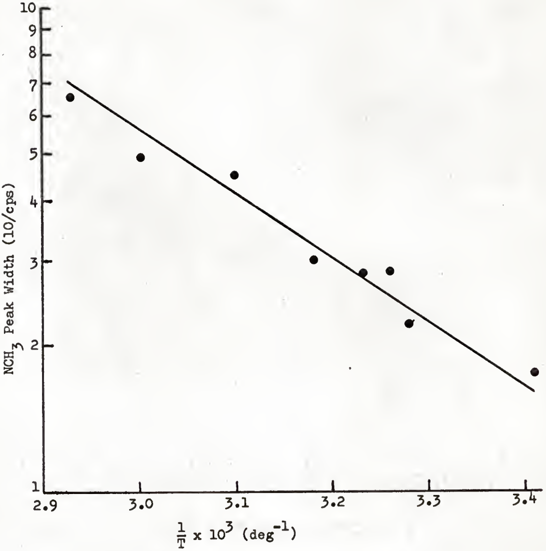

Figure 10. Arrhenius plot for $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$.

the boron, the boron resonance was doubled by coupling to the hydrogen. The B-H coupling constant was found to be 99 ± 10 cps for trimethylborazine and 111 ± 10 cps for 1,3-diaza-2-boracyclohexane.

As was mentioned earlier, Hawthorne (22) has shown that the boron resonances for monomeric dialkyl aminoboranes are down-field from trimethylborate, while those for dimeric dialkyl aminoboranes are up-field from trimethylborate. The B^{11} chemical shifts of all the compounds in the present investigation are down-field from trimethylborate. Therefore, all the compounds in the present series must be in the monomeric form. Thus any non-equivalence of alkyl groups on boron or nitrogen cannot be due to dimer formation.

The B^{11} chemical shifts of the aminoboranes show a definite pattern which appears to be closely related to the substituents directly attached to the boron.

Whenever, in the course of an experiment, a substituent - shift relationship crops up, several questions occur to the investigator: are the effects of the substituents additive? Are the substituent effects a function of the electronegativity of the substituent, or are mesomeric effects important also? How important are steric effects?

Additivity of substituent effects.-To test the additivity of the shift effects, a set of relative shift contributions has been obtained. For example, by subtracting the average of the first three entries in Table 24 from the fourth entry of the same table, we obtain the following relative shift contribution for a pair of substituents: $(C_6H_5) - (CH_3) = +(1.3 \pm .9)$ ppm. Other sets can be obtained similarly. The sets of averaged relative shift contributions for the substituent pairs in our series of compounds are summarized in Table 25.

In obtaining these values, the effect of substitution on the nitrogen has been disregarded, as long as the first atom in the substituent is a carbon or hydrogen. Clearly, this is only a first approximation, as can be seen from the first three entries in Table 24. These three entries have the same formula, except for differing substituents on the N, yet the B^{11} chemical shifts differ appreciably more than the experimental error. This difference is attributed to the differing substituents on N.

When the substituent on the nitrogen is another boron, as in trimethyl borazine (Entry 22 in Table 24), its effect on the B^{11} chemical shift can no longer be neglected. Now the nitrogens influence the B^{11} chemical shift to a lesser extent, since each nitrogen is attached to two borons. Thus we have designated the nitrogen substituents in trimethylborazine as "N-."

TABLE 25
RELATIVE SHIFT CONTRIBUTIONS OF SUBSTITUENTS

Substituent Pair	Relative Shift Contribution (ppm)
(B) , (CH_3)	−2.8 ± 1.8
(C_2H_5) , (CH_3)	0.0
(n-C_4H_9) , (CH_3)	0.0
(C_6H_5) , (CH_3)	+1.6 ± .9
($CH=CH_2$) , (CH_3)	+4.7 ± 1.8
(H) , (CH_3)	+4.7 ± .4
(Cl) , (CH_3)	+6.9 ± .9
(N) , (CH_3)	+15.8 ± .9
(N_)*, (CH_3)	+12.4 ± .9

*The symbol N_ is used to indicate a nitrogen bonded to two borons.

Having a set of relative chemical shift contributions for pairs of substituents, one only needs to assign a shift value to one of the substituents to obtain a "shift scale." Conceptually it would be most satisfactory to select the boron substituent as the basis; however, only two compounds with boron were available to us (Entries 12 and 13 in Table 24), and the agreement between these was rather poor. For this reason CH_3 has been selected as our basis and assigned a shift contribution of ±0.0. Now with this assignment, Table 25 becomes a "shift scale" table.

To test the self consistency of additivity of the shift contributions of the B^{11} substituents, we need to select a zero of shift. Again we have used the first three entries in Table 24 to obtain the shift origin. Thus:

$$\text{Sum of substituent contributions} + \text{shift origin} = \text{observed shift}$$

$$(15.8 \pm .9)\ \text{ppm} + (0.0) + (0.0) + \text{Shift origin} = -27.6 \pm .9\ \text{ppm}$$

$$\text{Shift origin} = -43.4 \pm .9\ \text{ppm}\ .$$

Now we are in the position to reconstruct or "calculate" the chemical shifts of the other compounds in the series. The results of this effort are to be found in Table 26. The observed chemical shifts and the difference between calculated and observed shifts have also been included.

TABLE 26

SELF-CONSISTENCE OF ADDITIVITY OF THE SHIFT CONTRIBUTIONS OF B^{11} SUBSTITUENTS

B^{11} Substituents	B^{11} Shift (ppm from $B(OCH_3)_3$)		
	Observed	Calculated	Difference
$N(CH_3)C_6H_5$	-26.3±.1	-26.0± .9	+0.3
$N(CH_3)CH=CH_2$	-21.4±.05	-22.9±1.8	-1.5
$N(C_6H_5)CH=CH_2$	-21.3±.5	-21.3±1.8	0.0
$N(n-C_4H_9)Cl$	-20.7±.03	-20.7± .9	0.0
N(Cl)Cl	-12.2±.3	-13.7± .9	-1.5
$N(B)CH_3$	-32.2±.05	-30.4±1.8	+1.8
$N(B)C_6H_5$	-27.3±.1	-28.8±1.8	-1.5
N(N)H	- 7.1±.4	- 7.1± .9	0.0
$N(N)CH_3$	-11.8±.1	-11.8± .9	0.0
$N(N)C_2H_5$	-12.0±.02	-11.8± .9	+0.2
$N(N)n-C_4H_9$	-12.5±.1	-11.8± .9	+0.7
$N(N)C_6H_5$	- 9.7±.7	-10.2± .9	-0.5
$N(N)CH=CH_2$	- 8.9±.1	- 7.1± .9	+1.8
N_(N_)H	-14.0±.2	-13.9± .9	+0.1

The agreement between observed and calculated chemical shifts is quite satisfactory. In no case is the difference more than twice the deviation from the mean in the average value of the chemical shift of the first three entries in Table 24. Since this average has been used in the calculation of both the relative shift contributions and the shift origin, the agreement between the observed and the calculated shifts is quite good. Thus the shift contributions of the substituents are additive.

B^{11} shift and inductive - mesomeric effects of the substituents.-Inspection of Table 25 shows that the relative shift contribution of the substituents gives an order opposite from that expected from electronegativity-inductivity considerations. A purely electrostatic picture of shielding predicts increased shielding, hence increased shift, with decreased electronegativity of the substituent. Clearly this is not the case for our aminoboranes; therefore, mesomeric effects of the substituent must be important. Indeed, the relative shift contributions in Table 25 do follow the M+ order of the substituents, with the possible exception of hydrogen.

A plot of the B^{11} shifts versus the sum of the Pauling electronegativities of the first atom in the substituent makes up Figure 11. In our series of compounds, one substituent is always nitrogen. For the other substituents the first atom has been indicated next to each point on the plot.

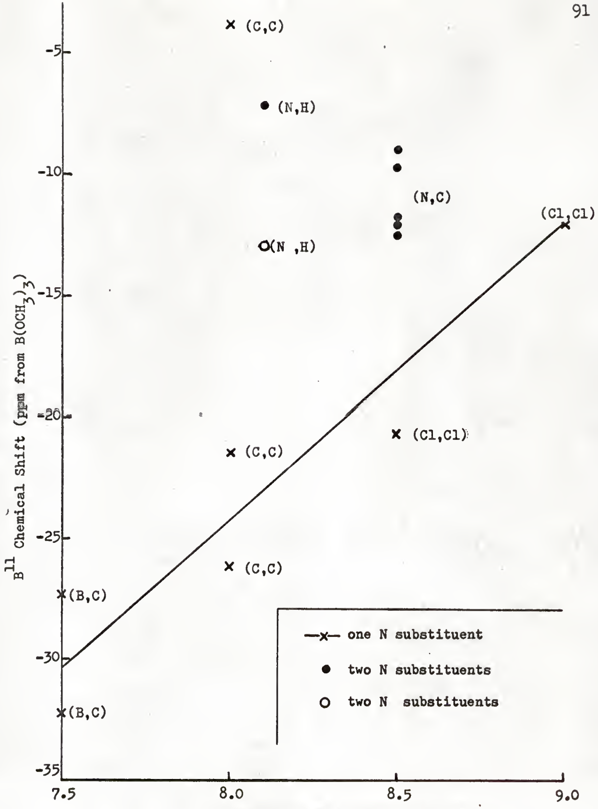

Figure 11. Boron shift dependence on substituent electronegativities.

According to Figure 11 only a rough relationship exists between the shifts and the sum of the electronegativities. The points of the plot fall into two groups: points for compounds with only one nitrogen on the boron and points for compounds with two nitrogens on the boron. For a given electronegativity, the compounds with two nitrogens are always more shielded than the ones with only one nitrogen. This indicates that increased π-bonding between the boron and the substituent is rather effective in shielding the boron. One expects, and apparently obtains, more double bond character between boron and nitrogen than between boron and either chlorine or an unsaturated hydrocarbon.

For the group of compounds with two nitrogen substituents there are too few data points to be able to say whether the shielding increases or decreases with increasing electronegativity of the substituents. For the compounds with only one nitrogen, there are enough data points to indicate that the shielding increases with increasing electronegativity of the substituents. This behavior is just the opposite to what one would expect from a purely electrostatic picture of shielding. Therefore, mesomeric effects must contribute to the shielding of the boron. Indeed, by inspecting the substituents, we see that the ease with which they form a double bond with boron, Cl $\rangle$ C $\rangle\rangle$ B, predicts the correct direction for the observed shielding.

Thus for the aminoboranes studied, any B^{11} shift and substituent electronegativity correlation that may exist is overshadowed by the mesomeric effects of the substituents.

Importance of steric effects.-It is interesting to note that the vinyl group causes greater shielding of B^{11} than does the phenyl group. (Cf. Entries 4-7, 18, 21 in Table 24.) Apparently the vinyl group is more effective in its mesomeric contribution than is the phenyl group, or the vinyl group induces a greater N-B double bond character. Actually, this is not surprising, since one expects that it is easier for the vinyl group to conjugate with the N-B partial double bond, than it is for the phenyl group to do so. For most effective conjugation the plane of the phenyl ring or the plane of the vinyl carbon-carbon bond has to lie in the plane of the N-B bond. Now it is easier for the vinyl group to attain this desired configuration than it is for the bulky phenyl group to do so, as can be seen from Stuart-Briegleb models of $(CH_3)_2N-B(C_6H_5)CH_3$ and $(CH_3)_2N-B(C_6H_5)CH=CH_2$.

That steric effects are quite important in determining the amount of double bond character between boron and a substituent, can be seen from 9,10-azaboradecalin (Entry 23, Table 24). The B^{11} shift of this compound is the highest in the series, namely -(3.8 ± .02) ppm, even though both the N and the B have only aliphatic substituents. (Cf. Entries 1-3, Table 24.) In Figure 1, the point for 9,10-azaboradecalin is way off the line drawn through the points for the other compounds with one nitrogen. It is proposed that the steric configuration of the two rings promotes the N-B double bond character and hence increases the shielding of the boron. A Stuart-Briegleb model of 9,10-azaboradecalin shows that rotation about the N-B bond is restricted to very small angles, while in the model of $(C_2H_5)_2N\text{-}B(C_2H_5)_2$ rotation is rather free.

In the single-ring aminoboranes (Entries 14-21, Table 24) steric effects must be negligible in going from a six-membered to a seven-membered ring, as can be seen from the almost identical shifts of the apirs of Entries 15 and 19, 16 and 20, 17 and 21.

CONCLUSIONS AND SUMMARY

Restricted Rotation About the N-B Bond

Separate peaks for the *cis*-*trans* isomers have been observed in all the proton spectra, except in the spectrum of $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$. Even in this compound the $=CH$ and NCH_3 peaks show considerable broadening below room temperature. Since merging of the separate peaks of the *cis*-*trans* forms was not observed at the temperatures available, the barrier to rotation could not be determined for the aminoboranes of this study. From the narrowing of the broad NCH_3 peak at elevated temperatures, the barrier to rotation for $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$ was very roughly estimated at 60 kcal/mole, which is considerably greater than the barriers to rotation quoted in the literature.

Anisotropy of the Substituent

Different shielding of the *cis* and the *trans* BCH_3 was observed when the substituent on nitrogen was a cyclopropyl group. This was the first time non-equivalence of the BCH_3 peaks has been observed when there was no phenyl on the nitrogen.

Non-equivalence of the NCH_3 protons was observed when the substituent on boron was a vinyl. Again, this was the first time that non-equivalence of NCH_3 has been reported when the boron substituent was a vinyl.

Thus, cyclopropyl and vinyl have been found to be sufficiently anisotropic to cause observable shift differences of aminoborane substituents.

Effect of the Substituent on the Barrier to Rotation

The stabilization of the N-B double bond by chlorine (9,10,15,17) has been confirmed in this investigation, since no merging or broadening of the non-equivalent NCH_3 peaks for $(CH_3)_2N\text{-}B(CH_3)Cl$ or $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$ was observed.

The vinyl group also raised the barrier to rotation about the N-B bond, since merging or broadening of non-equivalent NCH_3 peaks was not observed for $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$, and $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$. The effect of the vinyl group was felt on the B^{11} shifts also, since the vinyl shielded the boron noticeably more than the phenyl. As was mentioned earlier, this could be due to either the mesomeric effect of the vinyl or to the increased N-B double bond character when vinyl is attached to boron.

That the phenyl group lowers the N-B double bond character (9,17), seems to be borne out by the temperature dependence of the spectrum of $CH_3(C_6H_5)N-B(C_6H_5)CH=CH_2$. This is the only compound with vinyl on the boron where rapid interconversion of isomers was attained, as indicated by the sharpening of the broad $\dot{N}CH_3$ peak at elevated temperatures. The different behavior of this $BCH=CH_2$ compound is attributed to the presence of the two phenyl groups.

It is curious to note that the barrier to restricted rotation about the N-B bond is raised whenever there is an O (6), Cl (9,10,15,17 present work) or $CH=CH_2$ (present work) on the boron. All these substituents could form a double bond with the boron and thus compete with the N-B double bond formation. Apparently this is not the case, since these substituents increase the energy barrier, probably by resonance stabilization.

The presence of vinyl among the substituents - Cl, O, and $CH=CH_2$ - which stabilize the N-B bond is most significant. Chlorine and oxygen could increase the N-B double bond character by their inductive influence. The electronegativity of the vinyl group, however, is not significantly different from that of the alkyl or particularly the phenyl group. Therefore, increase in the N-B bond stability in the case of the vinyl substituent indicates resonance stabilization throughout the conjugated system.

Solvent Effects on the Barrier to Rotation

For the two compounds, $C_3H_5(H)N\text{-}B(CH_3)_2$ and $CH_3(C_6H_5)N\text{-}B(C_6H_5)CH{=}CH_2$, for which the barrier to rotation was low enough to see changes in the spectra at elevated temperatures, the solvent d_6-DMS removed the non-equivalence. Presumably the oxygen of the solvent forms a strong enough dative bond with the boron so as to reduce the N-B double bond character to the point where non-equivalence could no longer be observed.

For the other two compounds of this series which did not decompose in d_6-DMS, $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ and $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$, d_6-DMS did not remove the non-equivalence. Apparently in these compounds the intramolecular N-B dative bond is too strong to be appreciably affected by intermolecular B-O bonding. Since both of these compounds contain vinyl on the boron, the lack of solvent effect in DMS is further proof of the N-B bond stabilization by vinyl.

The mildly acidic solvent, $CDCl_3$, did not affect the barrier to rotation in any of the aminoboranes that were studied in this solvent.

Chemical Shift of the Substituents and Bonding in the Aminoboranes

The temperature may affect the proton chemical shifts of the substituents in several ways. If the double bond character of the N-B linkage is reduced, the substituents on N should be more shielded, while those on B should be less shielded. If temperature changes alter the average spatial relationship between atoms of the molecule, the chemical shifts of the substituents may be altered. Such changes of the spatial relationships between the atoms can be accomplished by either excitations of vibrational and rotational modes or by changes in the bonding of the atoms. In turn, changes in bonding are expected to influence the electron distribution in the molecule.

Apparently, none of these effects were of appreciable magnitude for the temperature range available, since the careful temperatures studies of this investigation show no significant changes in the substituent chemical shifts. The largest change was observed for the NCH_3 chemical shift of $n\text{-}C_4H_9(CH_3)N\text{-}B(C_6H_5)CH{=}CH_2$ in $CDCl_3$ solution. Here the NCH_3 shift increased 0.1 ppm with a decrease of 80°C in the temperature. Even this change is only two-to-three times as great as the experimental scatter. Again, the lack of temperature effects on the substituent shifts points to fair bonding stability in these aminoboranes.

The chemical shifts of the substituents were somewhat more sensitive toward solvent changes than to temperature changes. Dimethylsulfoxide is supposed to reduce the double bond character of the N-B linkage and thus increase the shielding of the N substituents. Indeed, a slight increase in the NCH_3 shift is always observed, when shifts in the CCl_4 and DMS solutions are compared.

If there is strong acid-base pair formation between the B of the solute and the O of the solvent, the BCH_3 are expected to be more shielded in DMS solution. Since the BCH_3 shift of $(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$ is the same in d_6-DMS solution as it was in CCl_4, double bond formation between the oxygen of the solvent and the boron of the solute is less strong than intramolecular double bond formation between the nitrogen and the boron of the solute.

The solvent $CDCl_3$ acts as a hydrogen donor in hydrogen bond formation. To the extent that hydrogen bonding reduces the N-B double bond character of the aminoborane in $CDCl_3$ solution, the nitrogen and its substituents gain electron density. This would tend to increase the shielding of the nitrogen substituents. But to the extent that the nitrogen forms a hydrogen bond with the D, the nitrogen and its substituents lose electron density. This decreases the shielding of the nitrogen substituents. Apparently, the first mentioned effect of $CDCl_3$ is more important for

$(CH_3)_2N\text{-}B(CH_3)CH{=}CH_2$, $(CH_3)_2N\text{-}B(C_6H_5)CH{=}CH_2$, and $(CH_3)_2N\text{-}B(n\text{-}C_4H_9)Cl$, since the NCH_3 shifts for these compounds increase in $CDCl_3$ solution as compared to the shifts in CCl_4 solution. For $CH_3(n\text{-}C_4H_9)N\text{-}B(C_6H_5)CH{=}CH_2$, however, the NCH_3 shift decreases in $CDCl_3$ solution as compared to the shift in the CCl_4 solution.

Effect of Substituents on the B^{11} Shift

The effects of the substituents on the boron shifts have been found to be additive. These effects follow the mesomeric rather than the inductive order of the substituents. Steric effects of the substituents are important, in particular for cases where the steric effect influences the N-B double bond formation.

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BIOGRAPHICAL SKETCH

Katherine Násfay was born in Budapest, Hungary, on January 1, 1932. She attended elementary schools in Hungary until early 1945, at which time she fled with her family from Russian occupation to Bavaria. In Bavaria she attended secondary schools in Simbach/Inn from 1946 to 1949.

In 1949, Miss Násfay emigrated with her family to the United States. She obtained her high school equivalency diploma in Greenwich, Connecticut, in 1950. From 1950 to 1952, she attended the University of Pennsylvania as a chemistry major. In 1952, she married Thomas A. Scott and moved to Cambridge, Massachusetts. For a year Mrs. Scott worked as a laboratory assistant for Skinner and Sherman, Inc., industrial chemists. In September, 1953, she entered Radcliffe College from which institution she obtained her B.A. in chemistry in 1955. She then worked as a chemist for Arthur D. Little, Inc., industrial consultants, until 1957.

From 1957, to 1959, Mrs. Scott took care of her young son, Jim. From 1959, to 1961, she worked part-time as a laboratory assistant in the Animal Nutrition Laboratory, University of Florida.

In 1961, Mrs. Scott entered the University of Florida as a graduate student in chemistry. She has worked as a graduate assistant in that department from 1961, to the present. In 1964, she received the degree of Master of Science. From 1964, until the present time, she pursued her course of study toward the degree of Doctor of Philosophy.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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